PB90-263856

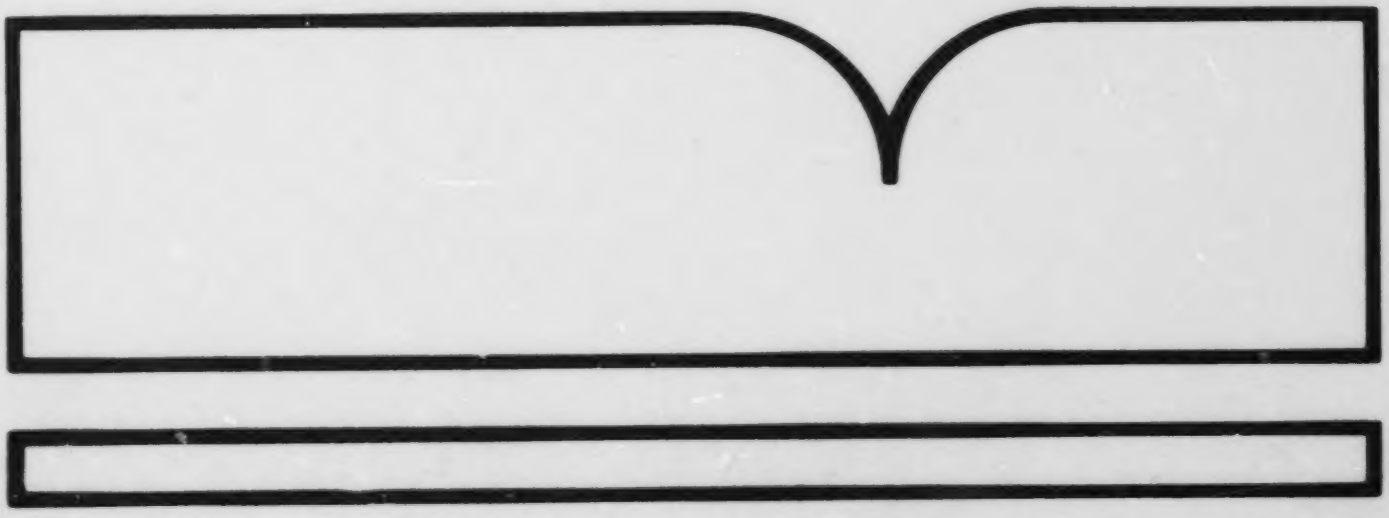
Fundamental Approach to Service Life Prediction of Flexible Membrane Liners (FML's)

Drexel Univ., Philadelphia, PA

Prepared for:

Environmental Protection Agency, Cincinnati, OH

Aug 90



U.S. Department of Commerce
National Technical Information Service
NTIS

EPA/600/2-90/041
August 1990

PB90-263856

FUNDAMENTAL APPROACH TO SERVICE LIFE PREDICTION OF FLEXIBLE MEMBRANE LINERS (FML'S)

by

Arthur E. Lord, Jr.
Department of Physics and Atmospheric Sciences
Drexel University
Philadelphia, PA 19104

and

Robert M. Koerner
Department of Civil Engineering
Drexel University
Philadelphia, PA 19104

Cooperative Agreement CR 810977

Project Officer

Paul de Percin
Municipal Solid Waste and Residuals Management Branch
Risk Reduction Engineering Laboratory
Cincinnati, Ohio 45268

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before complet

1. REPORT NO. EPA/600/2-90/041	2.
3. PB90-263856	
4. TITLE AND SUBTITLE Fundamental Approach to Service Life Prediction of Flexible Membrane Liners (FML's)	5. REPORT DATE August 1990
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Arthur E. Lord, Jr. and Robert M. Koerner	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Drexel University Philadelphia, PA 19104	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. CR-810977 WP#85060D
12. SPONSORING AGENCY NAME AND ADDRESS Risk Reduction Engineering Laboratory - Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED Complete
	14. SPONSORING AGENCY CODE EPA/600/14
15. SUPPLEMENTARY NOTES Robert E. Landreth (513) 5697871 FTS: 684-7871	

16. ABSTRACT

Predicting the service life of flexible membrane liners (FML's) exposed to chemicals has usually been done by physical or mechanical changes after exposure. The report summarized here presents an alternative approach--that of mass transport measurements. FML's exposed to four different chemicals and to water for periods up to 15 months were tested by five different mass transport related measurements. The results indicated that monitoring the transport properties of FML's exposed to particular chemicals over a reasonable exposure time could be considered as one possible method for predicting an FML's lifetime.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 87
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Cooperative Agreement No. CR 810977 with Drexel University. It has been subject to the Agency's peer review and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The prediction of the service life of flexible membrane liners (FMLs) when exposed to chemicals has usually been by way of testing for physical or mechanical property changes after periodic exposure times. This paper presents an alternate approach by evaluating the properties via five different mass transport related measurements of the exposed FML. These tests are water vapor transmission (WVT), radioactive tracer transmission (RT), water absorption (WA), water vapor absorption (WVA), and benzene absorption (BA).

This approach was tested for exposures of up to 15 months. The FMLs used were polyvinyl chloride (PVC), ethylene-propylene-diene monomer (EPDM), chlorinated polyethylene (CPE), and high density polyethylene (HDPE). The chemicals used were 10% sodium hydroxide (in water), 10% sulfuric acid (in water), 10% phenol (in water), 100% xylene, and water (as a control). The WVT and RT were found to be quite reliable test methods, whereas the WA and WVA techniques experienced serious problems in regard to obeying simple one-dimensional diffusion theory. The BA method worked well for HDPE. The various transport coefficients showed all the expected types of behavior with chemical exposure: (1) constancy with exposure (acids and bases on most all FMLs and all chemicals on HDPE), (2) decrease with exposure (plasticizers leaching from FMLs), and (3) increase with exposure (phenol-treated CPE). The WVT and RT results were generally complimentary to one another. The transport approach was quite successful in predicting the instability of CPE exposed to phenol. This instability was further verified by differential scanning calorimetry measurements.

The work reported herein lends credence to the use of mass transport measurements to determine structural change in FMLs. Thus the monitoring of transport properties, over a reasonable exposure time to particular chemicals, could serve as the basis for a predictive method for FML lifetime.

Also the method is proposed to be used in the screening of possible FML's for landfill uses. It could compliment present mechanical and physical property testing as in EPA 9090 chemical compatibility testing.

This report covers a period from 6 September, 1983 to 3 June, 1986.

CONTENTS

	Page
Foreword	iii
Abstract	iv
Figures	vii
Tables	x
Acknowledgments	xi
1. Introduction	1
2. Summary and Conclusions	5
3. Recommendations	6
4. Possible Service Life Prediction Testing for Flexible Membrane Liners	8
5. Experimental Design	11
Conditioning of Samples	11
Water Vapor Transmission (WVT)	14
Water (Liquid) Uptake to Determine the Diffusion Coefficient (WA)	18
Water Vapor Absorption to Determine the Diffusion Coefficients (WVA)	20
Radioactive Tracer Measurements to Determine the Diffusion Coefficients (RT)	25
Benzene Absorption to Determine Diffusion Coefficients (BA)	31
Microstructural Observations	31
Differential Scanning Calorimeter Measurements	31
6. Results of Mass Transport Measurements on Samples Exposed to Various Chemicals	32
Phase I (Up to six month exposure)	32
Water Vapor Transmission Results	32
Water Absorption and Water Vapor Absorption	32
Radioactive Tracer Measurements	37
Microstructural Observations	42
Differential Scanning Calorimeter Results	45
Phase II (Up to fifteen month exposure)	45
Water Vapor Transmission Results	50
Radioactive Tracer and Benzene Absorption Results	50
7. Quality Assurance	58

References 60

Appendices 63

A. Details of ASTM 96-80 WVT/Test 64
B. Actual Data from Water and Water Vapor Absorption Measurements 65
C. Actual Differential Scanning Calorimeter Data 74
D. Units Conversion Chart 76

FIGURES

Number		Page
1	Possible Long Term Exposure/Transport Data	9
2	Photographs of the Chemical Exposure Setups a) The Three Layer Plywood Boxes; b) Tub Distribution in One Box	12
3	Closeup Photograph of FML Folded into a Tub (Actually a Dish Pan)	13
4	The Water Vapor Transmission (WVT) Test a) Schematic of Vapor Cups; b) Photograph of Temperature and Humidity Controlled Chamber	15
5	Data from the WVT Test with 30 mil EPDM	16
6	Results of Experiments to Determine Loss Through Seals, a) PVC Gasket; b) EPDM Gasket Seals, with Aluminum Sheet Covering WVT Cup	17
7	Photograph and Schematic Diagram of the Apparatus for Determining the Absorption Rate of Water from the Liquid	19
8	General Solution for Mass Absorption Versus the General Diffusion Parameter $(Dt/l^2)^{1/2}$, where Diffusion is Perpendicular to Plate Thickness	21
9	Water Absorption Data for CPE at 30°C	22
10	Photograph and Schematic Diagram of the Apparatus for Determining the Absorption Rate of Water Vapor	23
11	Absorption Data of Water Vapor in 30 mil CPE	24
12	Photograph and Schematic Diagram of the Apparatus for Determining the Diffusion Coefficient Using Radioactive Tracers	26
13	Situation Involved for Diffusion of Radioactive Species from Top Surface	28
14	Data for Diffusion of Radioactive Benzene (^{14}C) in EPDM	29
15	Data Using Radioactive Tracers Illustrating Benzene (^{14}C) Diffusion Through EPDM	30
16	WVT Results for PVC as a Function of Exposure Time to Various Chemicals	33
17	WVT Results for EPDM as a Function of Exposure Time to Various Chemicals	34
18	WVT Results for CPE as a Function of Exposure Time to Various Chemicals	35

19	Water Uptake as a Function of Time for CPE Immersed in Water (As-received condition)	36
20	Water Vapor Uptake as a Function of Time for EPDM (Exposed to 10% H_2SO_4 for one month)	38
21	Diffusion Coefficient of Radioactively Tagged Benzene (^{14}C) in PVC as a Function of Exposure Time to Various Chemicals	39
22	Diffusion Coefficient of Radioactively Tagged Benzene (^{14}C) in EPDM as a Function of Exposure Time to Various Chemicals	40
23	Diffusion Coefficient of Radioactively Tagged Benzene (^{14}C) in CPE as a Function of Exposure Time to Various Chemicals	41
24	SEM Photographs of PVC-100X Magnification of Transverse Section	43
25	SEM Photographs of PVC-300X Magnification of Surface	44
26	SEM Photographs of PVC-3000X Magnification of Surface	46
27	Differential Scanning Calorimetry (DSC) Results for PVC as a Function of Exposure Time to Xylene. The ordinate represents the thermal power supplied to the sample to keep a constant temperature rise rate. The abscissa is the temperature of measurement. If the thermal power rises (downward trend) then additional heat is needed in this temperature range to "excite" (activate) additional modes of motion of the solid sample.	47
28	Differential Scanning Calorimetry (DSC) results for CPE as a Function of Exposure Time to Phenol. The ordinate represents the thermal power supplied to the sample to keep a constant temperature rise rate. The abscissa is the temperature of measurement. If the thermal power rises (downward trend) then additional heat is needed in this temperature range to "excite" (activate) additional modes of motion of the solid sample.	48
29	WVT Results as a Function of Chemical Exposure Time for CPE (15 month exposure)	51
30	WVT Results for Various FML's as a Function of Water Exposure Time (15 month exposure)	52
31	WVT Results as a Function of Chemical Exposure Time for HDPE (15 month exposure)	53
32	Diffusion Coefficient Results as a Function of Chemical Exposure Time for CPE (15 month exposure)	54
33	Diffusion Coefficient Results for Varicus FML's as a Function of Water Exposure Time (15 month exposure)	55

34	Diffusion Coefficient Results as a Function of Chemical Exposure Time for HDPE (15 month exposure)	56
35	Actual "Raw" Differential Scanning Calorimetry (DSC) Data for PVC Exposed to Xylene	76
36	Actual "Raw" DSC Data for CPE Exposed to Phenol	77

TABLES

Number		Page
1	Typical Leachate Composition - Average Values for Eighteen Sites, after Chain and Dewall[1]	1
2	Common Flexible Membrane Liners	2
3	Main Properties of Flexible Membrane Liners	3
4	Recommendations for Future Work - Based on Results of Present Study	7
5	Reproducibility of Radioactive Diffusion Data	27
6	Diffusion Coefficients (in cm^2/sec) Found in This Study	42
7	Summary of WVT and RT Results for 6 Month Exposure	49
8	Summary of WVT, RT and BA Results for 15 Month Exposure	57

ACKNOWLEDGMENTS

The authors would like to thank the U. S. Environmental Protection Agency's Municipal Solid Waste and Residuals Management Branch, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, for supporting this work through Cooperative Agreement 810977. Our project officer, Mr. Paul dePercin, has offered a great deal of encouragement, advice and help. Thanks are also due Mr. Robert Landreth of EPA. We owe a debt to the graduate students at Drexel who helped with the work. They were Rob Swan, Eric Linhuldt and John Wood.

SECTION 1
INTRODUCTION

The magnitude of solid waste generation in the United States is extremely large. Estimates range from 200 to 400 million metric tons annually which consists of four separate classifications:

- municipal waste
- industrial waste
- hazardous waste
- low level radiation waste

While public and financial incentives are working to reduce the total, the amount is still large and disposal is often by landfilling.* The inherent danger in landfilling is that moisture within the solid waste and that falling via rainfall or snow melt combines to form a liquid called "leachate" which can have dangerous properties. A typical composition is shown in Table 1 which is the average from 18 landfill sites.[1]

Table 1 - Typical Leachate Composition - Average Values for Eighteen Sites, after Chain and Dewall[1]

COD	40 to 90,000 units
BOD	80 to 33,000
TOC	250 to 28,000
pH	3.7 to 8.5
TS	0 to 59,000
TDS	600 to 55,000
TSS	10 to 70
Conductance	3,000 to 17,000
Alkalinity ($CaCO_3$)	0 to 21,000
Hardness ($CaCO_3$)	0 to 23,000

Hazardous waste landfills obviously have their own unique leachates. Unless contained, this leachate moves gravitationally until it mixes with the groundwater or surface water, and then flows hydrodynamically into the downstream water regime. Here it can easily be picked up by wells or mixed in water supply systems with undesirable results. Obviously, there exists a compelling need to prevent downstream contamination, using a liner or liner system.

Landfill liners can be placed in two general categories, rigid and flexible with general reviews of the entire area being presented by Kays[2] and Koerner[3]. The rigid liner category of concrete, shotcrete, gunite, soil cement, asphaltic concrete and bituminous panels is well developed, but is limited to nearly ideal sites. In general, these sites should be extremely stable and experience relatively low temperature fluctuations. Since this is usually not the situation, flexible liners have been used to a great extent.

*It is estimated that more than 80% of all solid waste is landfilled at present.

Flexible liners of compacted soils, chemically treated soils and blended bentonite clays are the natural materials available. Of these, bentonite clays with hydraulic conductivities (permeabilities) of 10^{-7} to 10^{-9} cm/sec* are the most widely used. Depending upon the head of liquid that is anticipated, clay liner thickness for landfills usually range from 2 ft to 10 ft. This is required for both the bottom and the sloping sides of the landfill. Obviously, such a thickness for the liner itself takes considerable volume away from the space available for the landfill material. An additional disadvantage arises because several chemicals severely deteriorate the clay soil structure. Anderson, et al.[4], have found that most organic solvents, e.g., acetic acid, aniline, methanol and xylene, increase the permeability by orders of magnitude with as little as 0.5 pore volumes moving through the clay.

This deterioration of the clay was probably somewhat responsible for the July 26, 1982 EPA regulations as stated below:

> "Prevention (via synthetic membrane liners); rather than minimization (via clay liners), of leachate migration similarly produces better environmental results in the case of surface impoundments used to dispose of hazardous wastes. A liner that prevents rather than minimizes leachate migration provides added assurance that environmental contamination will not occur**."

Indeed this series of events has ushered in an increased interest, use and awareness of flexible membrane liners (FML's).

Flexible membrane liners (FML's) come under no authorized name and have been called by many, e.g., synthetic membrane liners, polymeric liners, pond liners, and geomembranes. They are generally made of polymerized resins (thermoplastics) or vulcanized rubbers and sometimes combinations of both. There are also hybrid systems, such as sprayed geotextiles which are generally directed toward specific applications. Table 2 lists the most common flexible liners.

Table 2 - Common Flexible Membrane Liners

- Thermoplastics (Plastics)
  - polyvinylchloride (PVC)
  - polyethylene (LLDPE, MDPE, HDPE)
  - chlorinated polyethylene (CPE)
  - elasticized polyolefin (3110)
- Rubbers
  - butyl rubber
  - epichlorohydrin rubber
  - ethylene propylene diene monomer (EPDM)
  - chlorosulphinated polyethylene (hypalon)
  - polychloroprene (neoprene)
  - ethylene propylene terpolymer (EPT)

---

*Conversion factors to MKS (SI) units are found Appendix D

**parenthesis added

Table 2 - Continued

- Combinations
  - PVC - nitrile rubber
  - PE-EPDM
  - PVC - ethyl vinyl acetate
- Hydrid Systems
  - bitumen impregnated geotextile
  - bitumen/rubber impregnated geotextile

Each of these liners has its own characteristics and properties which are important to any specific installation. They must be recognized as having unique physical, mechanical, chemical, transport, thermal and biological properties, some of which are listed in Table 3 following:

Table 3 - Main Properties of Flexible Membrane Liners

- Physical
  - thickness
  - specific gravity
  - weight
  - hardness
- Mechanical
  - technical strength at break
  - tensile strength at yield
  - elongation at break
  - elongation at yield
  - modulus of elasticity
  - tear propagation (tongue or trapezoidal)
  - impact resistance (Spencer)
  - hydrostatic resistance (like Mullen burst)
  - soil to liner friction (direct shear)
  - seam strength (shear and peel)
  - ply adhesion
- Chemical
  - compatibility to waste material
  - volatile loss
  - ozone resistance
  - ultraviolet resistance
  - stability to various pH liquids
  - environmental stress cracking/rupture
- Transport
  - permeability
  - diffusion
- Thermal
  - specific heat
  - transitions (melting, freezing, glass, etc.)
  - resistance to temperature extremes
- Biological
  - stability to microbe attack
  - general burial resistance

Chemical compatibility is important with every liner system, but is critical in the case of hazardous waste landfills. Most liner manufacturers publish, or know of, chemical compatibility with specific chemicals but seldom know of the effects of mixtures and compounds as are common with hazardous waste leachates.* When this information is not available, complete immersion or one-sided tub tests of the candidate liners in the actual or synthesized leachate is necessary. The general procedure is set forth in the EPA 9090 test method. Uniform sized candidate liner samples are placed such that the incubating liquid is surrounding the samples and is left constant in its consistency. Ambient and/or elevated temperatures, (e.g., 50°C) are the usual targeted values. The liner samples are removed periodically (up to 120 days), dried and cut into test specimens. Usually weight and thickness, along with selected mechanical properties are evaluated. Based on the chemical exposure data, arbitrary standards are set up for "compatibility". For example a common (but not unique) criteria is no more than a 3% change in physical properties and no more than a 10% change in physical properties.** (These arbitrary standards are fraught with all sorts of obvious difficulties.) Until such compatibility data is available, and the proper liner selected that is compatible with the landfilling leachate, one cannot enter into the actual design process. Elements of this design process are given by Koerner.[5]

Note should be made, however, that this type of chemical compatibility testing is of a short term nature (possibly accelerated by increased temperatures) and does not include the use of stress. Needed is a long term method for service lifetime. This aspect of FML's is the thrust of the work to be reported here.

---

*A limited amount of proprietary work has been done by some membrane suppliers with specific leachates in certain FML's.

**It is doubtful that these changes are statistically-significant.

SECTION 2
SUMMARY AND CONCLUSIONS

The object of the present study was to determine if structural changes in flexible membrane liners (FML's) could be observed using relatively simple mass transport measurements. If such changes could in fact be monitored, the feasibility of using these techniques to predict FML lifetime was to be explored. A representative number of FML's were exposed to acids, bases, solvents, hydrocarbons and water (as a control) for periods up to 15 months.

The reproducibility of the identified measurement techniques on "identical" as-received or exposed samples was shown to be quite satisfactory for such a study. That is, any truly significant effect due to chemical exposure was well beyond the experimental uncertainty.

Both water vapor transmission and the radioactive method showed the well-known reduction in mass transport when plasticizer is leached from an FML. Both methods indicate that, in general, acid and base exposure has little effect on typical FML's.

In the case of chlorinated polyethylene (CPE) exposed to phenol, it was found that the mass transport increased significantly during exposure, and also the mass transport was continuing to rise at the 15 month mark. If this trend continued, and could be extrapolated, it would be possible to predict the time when the transport rate was unacceptably high i.e., to predict the FML's lifetime. Of course, this assumes that the upper acceptable limit is given. For all other combinations of FML and chemical, it appeared that no strong, continuing change in transport occurred due to chemical exposure.

The CPE exposed to phenol also showed strong development of "structure" in the differential scanning calorimeter (DSC) thermal responses. This indicated some kind of as yet unexplained change in the internal structure of the CPE. Unfortunately DSC results were not obtained on any of the other exposed FML's, except PVC exposed to xylene where the stiffening was most apparent with loss of plasticizer.

It should not be construed from the results presented that CPE has unique problems (or a general problem at all) with chemical stability. For the particular series of tests performed here, the CPE/xylene situation simply gave the most clear cut demonstration of a possible technique with which to determine a "mass transport lifetime".

It is suggested that transport measurements be included with physical and mechanical testing in the EPA 9090 chemical compatibility qualification testing for flexible membrane liners.

SECTION 3
RECOMMENDATIONS

As a result of the work done here it is felt that the following comments might be of definite importance in the general area of FML compatibility testing.

- Transport property measurements are viable alternatives (or complimentary) techniques to physical and mechanical property measurements for chemical compatibility testing and should be utilized in some manner.

- The authors feel that transport related measurements should be encouraged for parallel use in EPA 9090 experiments along with the usual measurements of changes in physical and mechancal properties. It is, in the final analysis, the transport of the waste leachate through the FML which is of paramount interest. It cannot be completely assessed by indirect methods as is currently done.

- The chemical exposure should be for a long period of time (certainly over a year) and under ambient type conditions (including stress). Short term, accelerated aging tests should be viewed with caution in the authors' opinion, for they do not simulate actual conditions in the field. Long term elevated temperatures (unless actually those found in the field) could lead to completely misleading physical and chemical changes in the FML.

- Of the three types of transport measurements recommended, water vapor transmission (WVT) radioactive tracer (RT) and benzene absorption(BA), we feel that the WVT is easiest to use and is an existing ASTM standard, but for HDPE the BA method is necessary. This technique as well as the RT technique should be further explored, documented and considered for a standard test procedure. Work should definitely proceed toward developing a simple, safe radioactive tracer method using radioactively "tagged" water (and not benzene) as the diffusant.[6,7]

- The use of other property measurements should be considered as a function of chemical exposure. Differential scanning calorimeter (DSC) results show significant change in the structure of CPE exposed to phenol. Also, obvious changes for de-plasticized PVC were picked up easily in the DSC work. DSC is only one technique to detect physical and chemical changes. One can also envision using infrared spectroscopy, gas chromotography, etc.

All of these suggestions are incorporated in Table 4.

Table 4 - Recommendations for Future Work - Based on Results of Present Study

SUGGESTION	REASON	CHANCE OF IMPLEMENTING	EXPENSES	INTERPRETAION	REMARKS
Require WVT* type measurements in 9090 testing *WVT - water vapor transmission	Transport is the property of direct interest - not mechanical or physical properties	Reasonably good - some labs are already doing WVT in 9090 testing Needs a rigorous test protocol	Not Prohibitive	Changes and trends are easy to see (if present) However 120 days may be too short to develop trends. Elevated temperatures may produce non-real effects	Same problems as with mechanical and physical properties However gives an additional piece of data which is more meaningful test for actual application
Develop radioactive tracer tests for water-like leachates. Tag water with tritium	Very difficult to seal HDPE in WVT cups well enough to measure true transmission rate	Reasonably good - if funding is sufficient to further develop method for this particular application. (There has been pertinent work done in this regard: references 6 and 7) Needs a standard procedure	Not Prohibitive	Same as above	Same as above. Most consultants reluctant to use radioactive materials
Extend 9090 - type tests to at least one year	The changes and trends developed in 120 days may not be true long term effects	No difficulty technically - but great difficulty in practice due to additional costs involved	Very Expensive (due to extra labor and space costs)	Easier to interpret data than in the shorter term tests, for the changes and trends will usually be more prounounced	May be too expensive
Use thermal measurements (e.g., DSC) in addition to the transport measurements Other techniques would also be considered	Could very possibly help corroborate findings of incompatibility found in transport measurements	Good tests are routinely performed in chemical laboratories	Not Prohibitive (if equipment available)	Not a direct test at all - to be used to corroborate other findings	Compatibility testing definitely needs a multitude of experimental techniques

SECTION 4
POSSIBLE SERVICE LIFE PREDICTION TESTING FOR FLEXIBLE MEMBRANE LINERS

There have been a number of long term exposure tests with FML's both in the laboratory and in the field.

Haxo and Nelxon[8] have exposed a number of geomembranes to municipal solid waste (for 56 months) and various hazardous wastes (up to 800 days). After exposure, various physical, mechanical or chemical tests were performed on the geomembranes and the results compared with the zero exposure values. Bellen and Corry[9] immersed six geomembrane types in twenty chemical solutions for periods up to two years. Physical and mechanical properties were measured after exposure and compared to as-received values to determine possible degradation effects. A study concerning the effect of chemical exposure on seams has also been performed.[10] Chemical exposures of up to one year were performed. Some very short term creep testing of seamed materials was performed in air at 50°C. Except for the creep tests, none of this work[8,9,10] involved stressing of the FML's during exposure.

Haxo and coworkers at Metrecon have looked at the mechanical, physical and certain chemical properties of samples retrieved from actual landfills and holding ponds.[11-17] The properties are compared with original material wherever possible. This is the most extensive listing of property values of field exposed FML's known to the authors. There is however no attempt at prediction of service life. One extreme difficulty in this area is that there are no universally accepted standards for property values in the FML area, and thus there is no totally accepted way of determining allowable property changes.

It should be mentioned that the natural gas transportation industry utilizes polyethylene (PE) pipe, and a great deal of effort has gone into the long term testing of the pipe material.[18-21] The lifetime of the pipes is determined as a function of the internal pressure. This lifetime/pressure plot can be extrapolated to the desired service lifetime and the design stress determined. There appears to be no analogous long term lifetime testing in the geomembrane area, at least in the United States.

The approach in the present study is to determine transport properties (permeability and diffusion) as a function of exposure time to various simple chemicals. The time-dependent trends in the transport property will be used as an indicator of the material's stability, and extrapolation to predict lifetimes will be considered. It should be emphasized that the transport properties are the quantities of most direct interest in any containment function application and physical and mechanical properties, although certainly related to the transport properties, are of secondary importance. Typical test data might look like the that shown in Figure 1.

If values for the highest permissible transport coefficients were available, then it would be a simple matter to extrapolate the data and predict a lifetime for the particular FML. Unfortunately, no accepted upper limits* are available for an FML's performance and also extrapolation is

*It, of course, must be realized that the public at large wants absolutely zero leakage. In all truthfulness, this can probably never be achieved, even in the most ideal of situations.

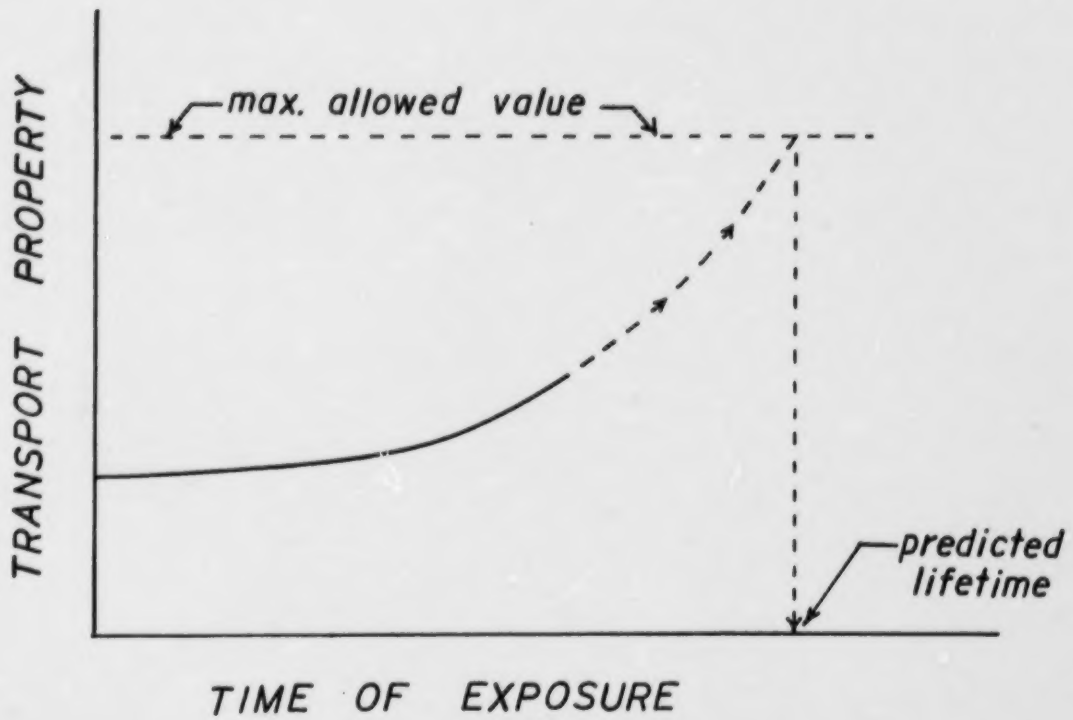


Figure 1 - Possible Long Term Exposure/Transport Data

certainly fraught with difficulty. Nevertheless, it appears that this approach has never been attempted before, and it is more viable than other approaches in that the direct property of interest (transport) is being evaluated in the exposure test.

SECTION 5
EXPERIMENTAL DESIGN

This section will have descriptions of the various techniques, including the theory necessary to analyze the data obtained. Also some typical data may be presented. It is felt that a self-contained experimental technique section is preferable compared to separate experimental and theory sections.

Conditioning of the samples will be discussed. The various experimental techniques will be dealt with separately. These include:

- water vapor transmission
- various diffusion techniques for both water and benzene
- microstructural observations
- differential scanning calorimetry.

CONDITIONING OF THE SAMPLES

It was decided after careful analysis of the existing literature, that the one-sided chemical exposure was the most realistic of treatments.[15] To this end five large boxes were constructed from 4 ft x 8 ft sheets of plywood, the final size of the boxes being 4 ft x 8 ft x 10 in. high. (Refer to Figure 2a for a photo of the boxes.) In each box 12 holes were cut, each large enough to accommodate a normal-sized plastic tub (actually a dish pan). (Refer to Figure 2b.) The FML was "form-fitted" into the dish pan (Figure 2b) resulting in the obtaining of three different types of samples:

- bottom area samples - no folds (0°)
- side samples - 1 fold (90°)
- corner samples - 2 folds (180°).

(See figure 3 for details.)

The various chemical solutions (to be enumerated later) were placed into the tubs and the cover was closed to eliminate the possibility of rain or snow filling the tubs, as the samples were exposed to the elements. The height of liquid in the tub was checked every few days and if evaporation loss occurred, more solution was added to achieve the initial height. (Concentration was however not checked).

At the end of the prescribed exposure time (varying up to fifteen months) the chemical was poured off into a holding bottle(s), and the FML sample taken out of the tub. The sample was allowed to dry for a few days under the box, was then cut up into smaller samples for the various transport tests. These samples were then put in plastic bags, which were mechanically sealed. Before performing the transport tests, some of the samples were vacuum dessicated until they reached a constant weight. This point will be discussed later.

The FML's chosen for the study were (all of a nominal 30-mil thickness):

- polyvinyl chloride (PVC) - a commonly used FML - a thermoplastic
- chlorinated polyethylene (CPE) - a commonly used thermoplastic
- ethylene propylene diene monomer (EPDM) - a commonly used thermoset rubber

(a)

(b)

Figure 2 - Photographs of the Chemical Exposure Setups a) The Three Layer Plywood Boxes; b) Tub Distribution in One Box

Figure 3 - Closeup Photograph of FML Folded into a Tub (Actually a Dish Pan)

- high density polyethylene (HDPE) - a commonly used thermoplastic, quite resistive to most chemicals.

The chemicals used were:

- water as a control
- 10% water solution of sulfuric acid - a strong acid solution
- 10% water solution of sodium hydroxide - a strong basic solution
- 100% Xylene - a common solvent
- 10% (by weight) water solution of phenol - a common and troublesome byproduct of many chemical processes

(See page 50 for the matrix of FML's and chemicals for the 15-month exposures).

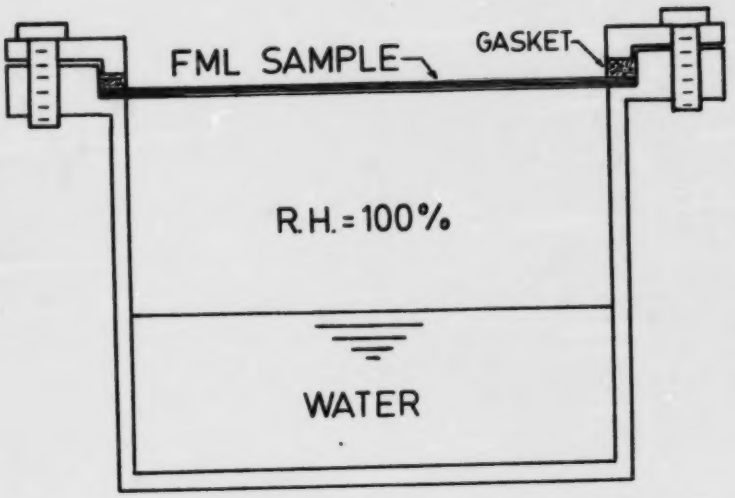
These FML's were also chosen to a certain extent because they were some of the ones being used in concurrent U. S. EPA projects. In this way degradation of the same FML's by the same chemicals could be monitored using different experimental techniques.

WATER VAPOR TRANSMISSION (WVT)

Water vapor transmission (WVT) tests were performed on the as-received and chemically-exposed samples to see if changes could be observed indicating instability of the FML structure. The WVT tests were run according to ASTM E-96-80. There are certain variations allowed in this procedure. The one used in the present study involved placing a certain amount of water in the bottom of an aluminum cup, mechanically-sealing the cup with the FML (30 cm^2 in area) and placing it in a constant temperature-constant relative humidity environment.

According to ASTM E-96-80, the temperature must be held to within ±1°F and the relative humidity to within ±2%. The commercial humidity/temperature chamber used here maintained these standards. The cup and humidity chamber are shown in Figure 4. (It was found in our work that mechanical seals worked much more reliably than the wax seals.) The weight loss is then determined as a function of time and from this data the WVT is determined. The weights were determined to the nearest 0.01 gram. The WVT is quite often given in units of gram/$(meter)^2$-day. See Figure 5 for typical data. The permeance and permeability can be obtained from the WVT. This procedure is outlined in Appendix A.

Work was done to determine if leakage of vapor around the mechanical seal was a problem. An aluminum sheet was used in this case as the closure. The aluminum was of the same thickness as a typical FML, i.e., about 1 mm. The aluminum sheet was sealed into place with a plastic or rubber gasket, which sealed the sheet to the cup. The standard ASTM E-96-80 WVT test was then performed. Figure 6 shows the results for a "PVC gasket" and for an "EPDM gasket". It is seen that after the initial setting time, there is no measurable loss of weight from the cup. Because the aluminum top sheet is totally impervious within the limitations of this test, it means that there is no measurable loss through the mechanical seal.



a) Schematic of Vapor Cups

Reproduced from
best available copy.

b) Photograph of Temperature and Humidity Controlled Chamber

Figure 4 - The Water Vapor Transmission (WVT) Test

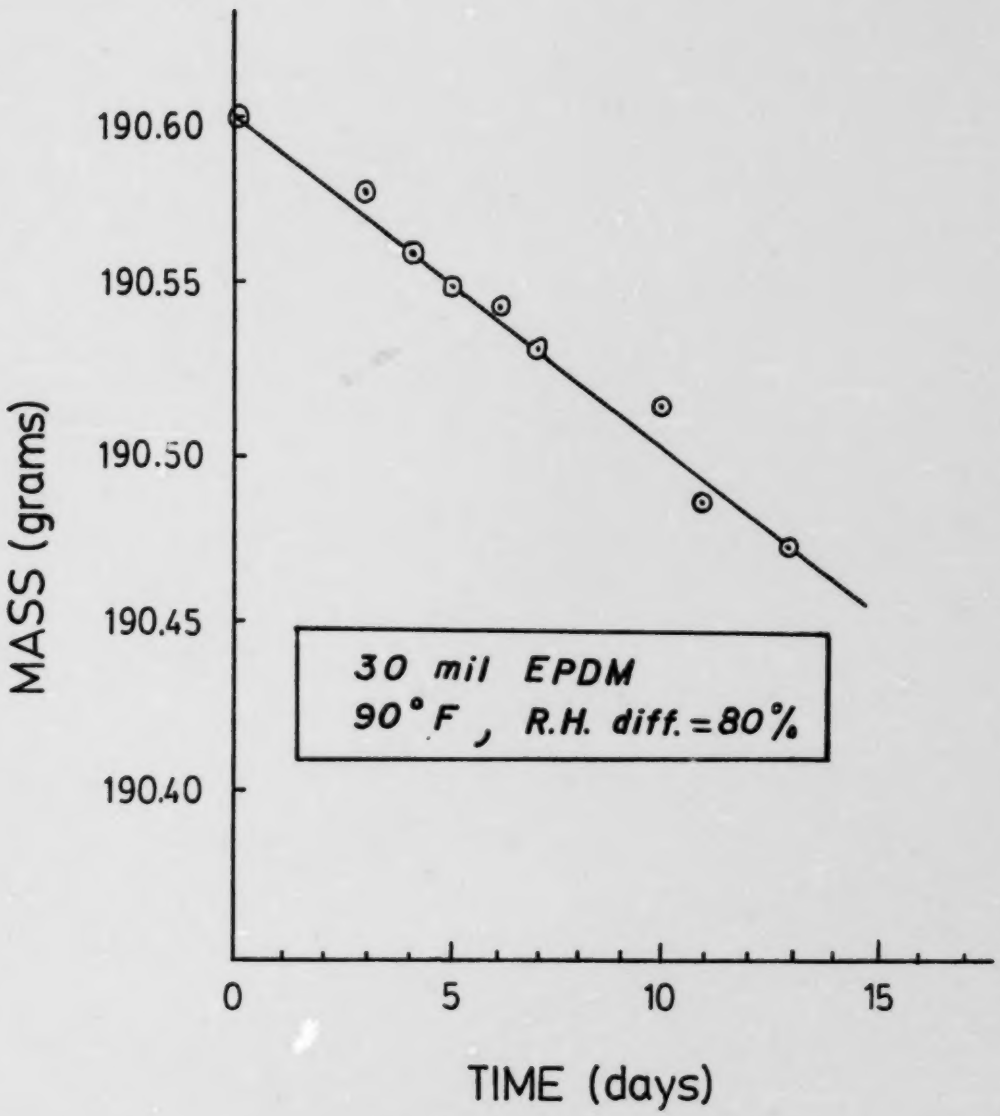


Figure 5 - Data from the WVT Test with 30 mil EPDM

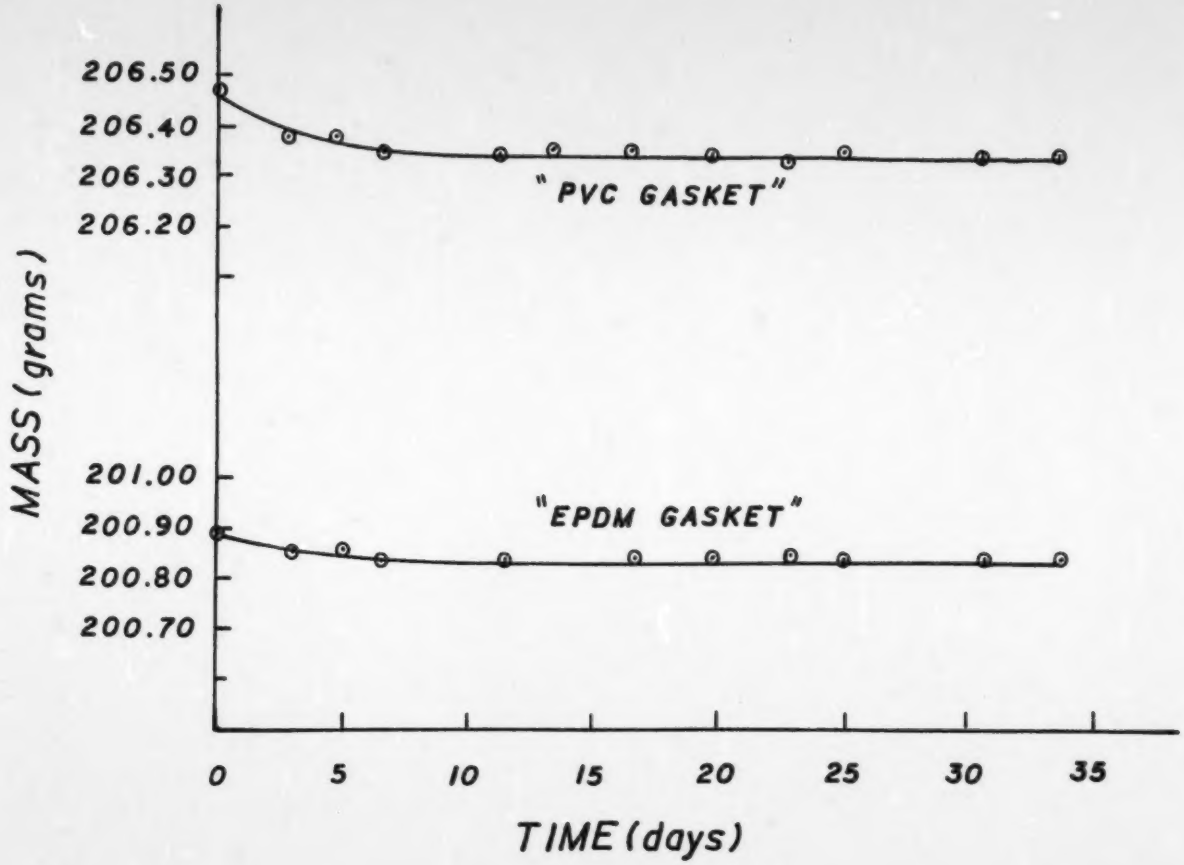


Figure 6 - Results of Experiments to Determine Loss Through Seals, a) PVC Gasket; b) EPDM Gasket Seals, with Aluminum Sheet Covering WVT Cup

Thus if weight can be measured to the nearest 0.01 gram, the standard area of 30 cm^2 is used and measurements are made for 30 days, the lowest possible WVT that can be determined is

$$\text{Lower Limit} = \frac{0.01 \text{ gm}}{0.0030 \text{ m}^2\text{-30 days}} = 0.11 \frac{\text{gm}}{\text{m}^2\text{-day}}^{*}.$$

Runs on many "identical" samples** showed that WVT results could generally be reproduced to within ±5%, with a very few being up to a maximum of ±10% different. This does not mean that the WVT of <u>any</u> FML sample will be within 5% of <u>any other</u> sample of the same type of FML. The WVT can change by considerably more than these reproducibility factors from lot-to-lot.[22]

WATER (LIQUID) UPTAKE TO DETERMINE THE DIFFUSION COEFFICIENTS (WA)

The diffusion coefficient of water in a particular FML can be determined by immersing the sample in water and monitoring the weight gain (i.e., the uptake) as a function of time. To determine the volume diffusion unequivocally, it must be assumed that surface absorption effects are negligible. [To clarify this point, refer to Crank and Park[23].]

The experimental procedure used in this section of the work is depicted in a photograph and schematic diagram in Figure 7. A large bath of distilled water is used. The glass bath container is approximately 30 cm in diameter by 30 cm high. The bath heater/circular unit holds the temperature of the bath to within ±0.2°C. The bath temperature is read to the nearest 0.1°C using a sensitive mercury thermometer. The samples of approximate size 10 cm x 4 cm x 0.1 cm (~4 grams) were placed in a vacuum dessicator until they reached a constant weight. They were then immersed directly in the bath and withdrawn at prescribed times for weighing. The weighing was done on an electronic digital balance and was reproducible to 0.01 grams. Before weighing, the samples were blotted dry on a paper towel until a constant weight was achieved.

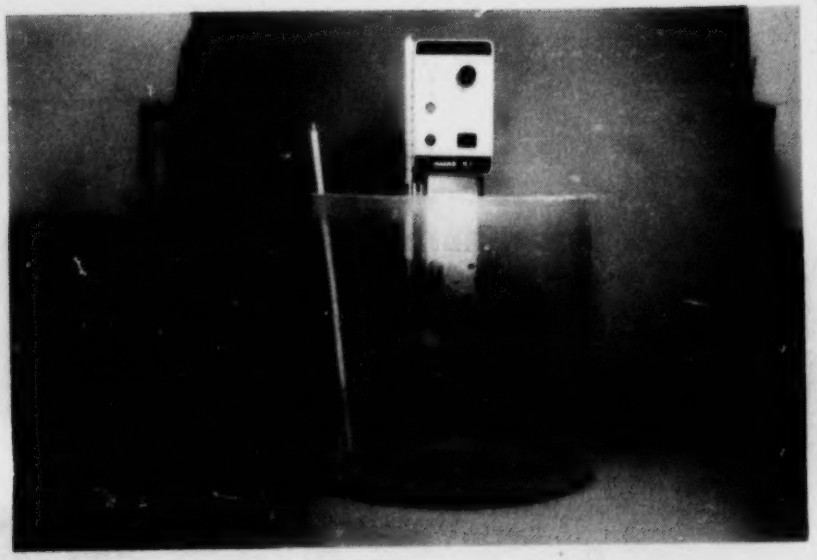
Assuming Fickian diffusion, standard theory is used to obtain the diffusion coefficient. The theory involved in the measurement assumes a wide, thin membrane with lateral dimension much larger than the thickness. The solution for the weight change, is as follows:[23,24]

$$\frac{M_t}{M_\infty} = 4\left(\frac{dt}{l^2}\right)^{1/2}\left[\frac{1}{\pi^{1/2}} + \sum_{n=1}^{n=\infty}(-1)^n \text{ ierfc}\left(\frac{nl}{2\,(Dt)^{1/2}}\right)\right] \quad (1)$$

---

*If a balance of reproducibility 0.001 gram would have been available, it is possible that this lower limit could have been reduced.

**"Identical" means the samples come from adjacent positions on the same FML roll, hopefully eliminating specimen differences as far as chemistry, porosity, mechanical properties, etc., are concerned.



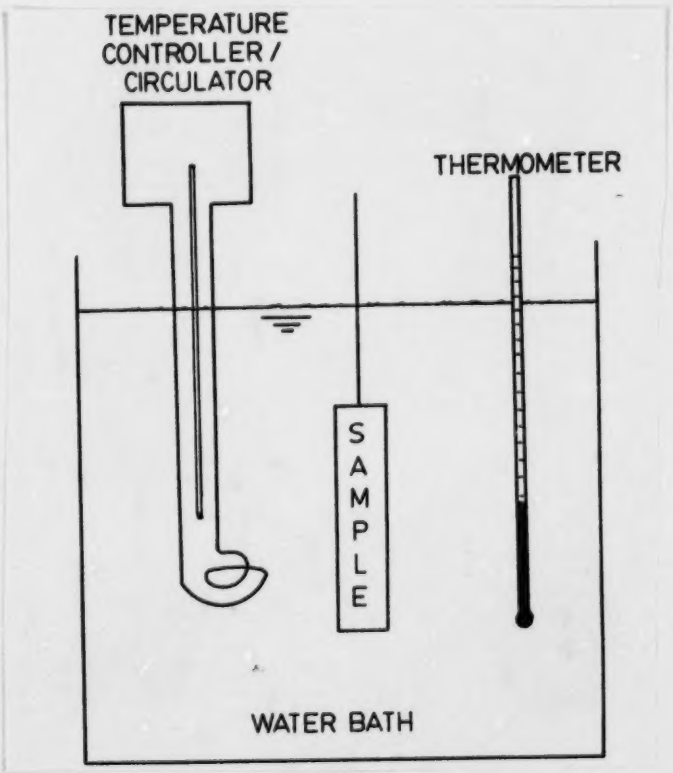
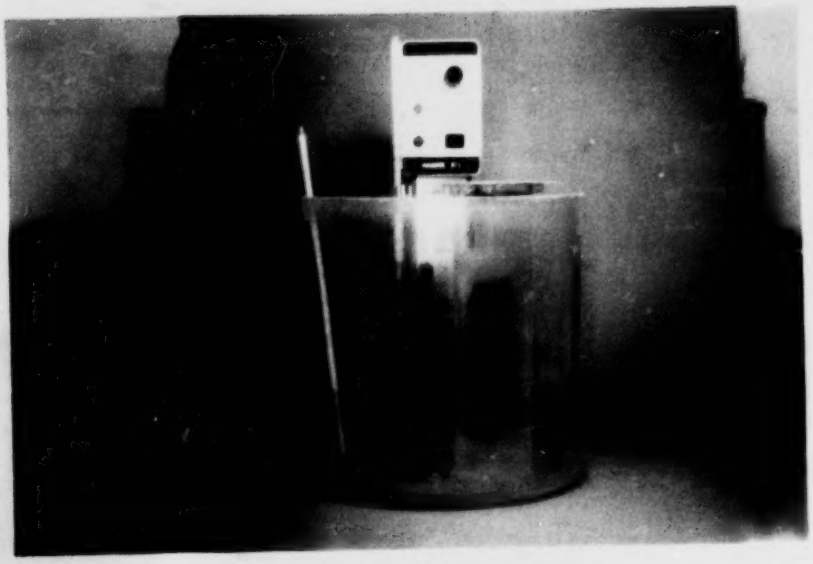


Figure 7 - Photograph and Schematic Diagram of the Apparatus for Determining the Absorption Rate of Water from the Liquid



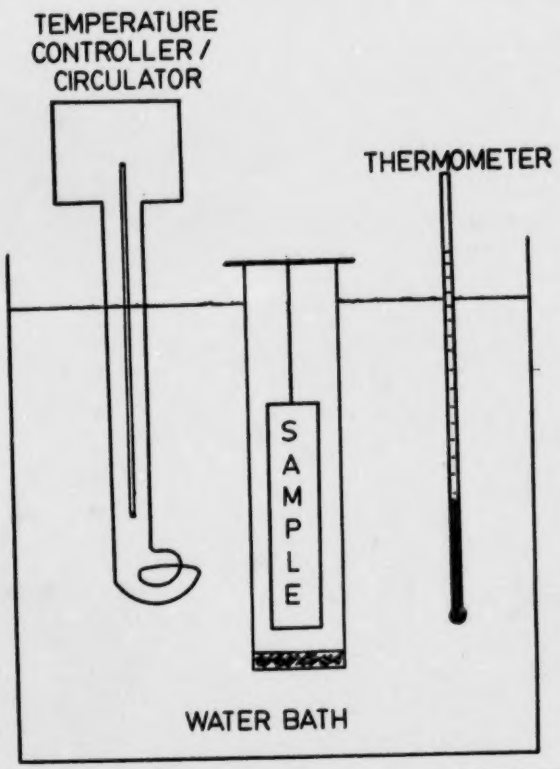


Figure 10 - Photograph and Schematic Diagram of the Apparatus for Determining the Absorption Rate of Water Vapor

where

M_t = the weight gain at time t

M_∞ = the weight gain at very long times, that is when the equilibrium concentration of diffusant is present

D = diffusion coefficient

l = half the thickness of the sample

ierfc = the integral of the error function.

Figure 8 shows the general solution of M_t/M_∞ for the dimensionless parameter $(Dt/l^2)^{1/2}$. The M_t/M_∞ time dependence is strictly $t^{1/2}$ up to a value of M_t/M_∞ approximately equal to 0.50. This occurs at a $(Dt/l^2)^{1/2}$ value of about 0.5 also. Note that it takes a very long time (with respect to the time for the break from the $t^{1/2}$ dependence to occur) for complete saturation to occur, i.e., the $M_t/M_\infty = 1.0$. Therefore, if t_{break} is known, the diffusion coefficient, D, can be obtained from the break of the curve of Figure 8. Figure 9 gives some data from this study for CPE in water at 30°C. Note the break in the curve for a time = 1.0×10^6 seconds (11.56 days). Therefore the diffusion coefficient for water into CPE is given as

$$\left(\frac{Dt_{break}}{l^2}\right)^{1/2} = 0.5$$

With l = 0.038 cm and $t_{break} = 10^6$ seconds, one obtains:

$$D = \frac{(0.5)^2 (0.038)^2}{10^6} = 2.9 \times 10^{-10} \text{ cm}^2/\text{sec.}$$

Also note from Figure 8 that it will take a value of $(Dt/l^2)^{1/2} \approx 2$ to obtain near-saturation. That is, it will take a time of order of $(2/0.5)^2 \times 10^6 = 1.6 \times 10^7$ seconds, or approximately 185 days to be able to determine M_∞. This makes the t_{break} approach very attractive from a logistical standpoint. Unfortunately this behavior is not seen in many of the liquid water diffusion tests performed during this study. This will be discussed later where reproducibility will also be discussed.

WATER VAPOR ABSORPTION TO DETERMINE THE DIFFUSION COEFFICIENT (WVA)

In precisely the same manner as with the liquid water absorption test just described, the use of water vapor as an absorbed gas can be used to obtain the diffusion coefficient. Again it is assumed that surface barrier effects are negligible. The theory is exactly the same as in the previous section and only a slight modification in the experimental setup is necessary. Now, instead of suspending a geomembrane directly in a controlled temperature bath, it is placed in a separate glass cylinder with water in the bottom which in turn is suspended in the water bath. (See Figure 10.) Thus 100% humidity conditions are present, and water vapor now enters the geomembrane as a function of time. The increase in weight is plotted against time as in Figure 11 which results in the following calculation: Using l = 0.038 cm and $t_{break} = 7 \times 10^5$ sec, one obtains

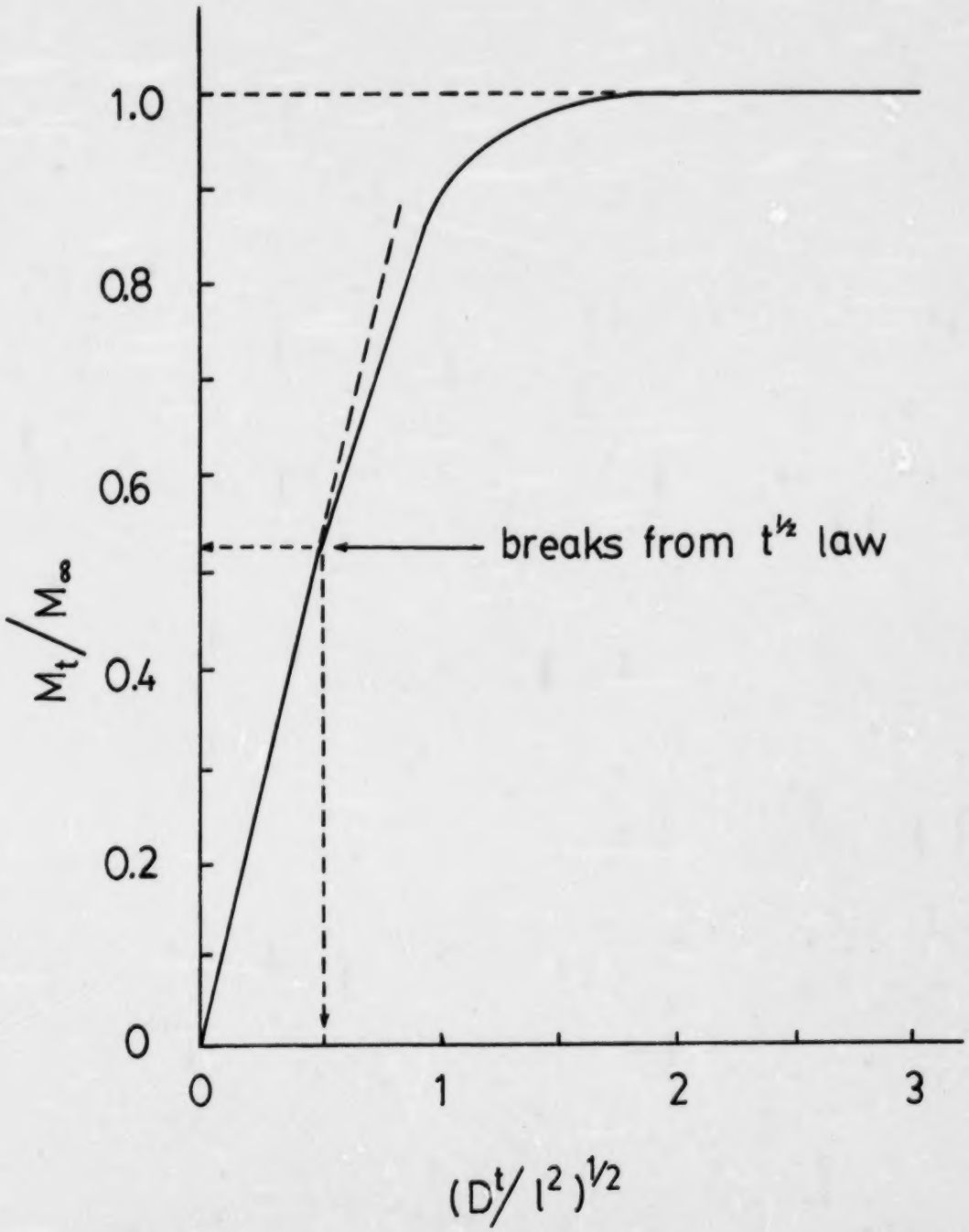


Figure 8 - General Solution for Mass Absorption Versus the General Diffusion Parameter $(Dt/l^2)^{1/2}$, where Diffusion is Perpendicular to Plate Thickness

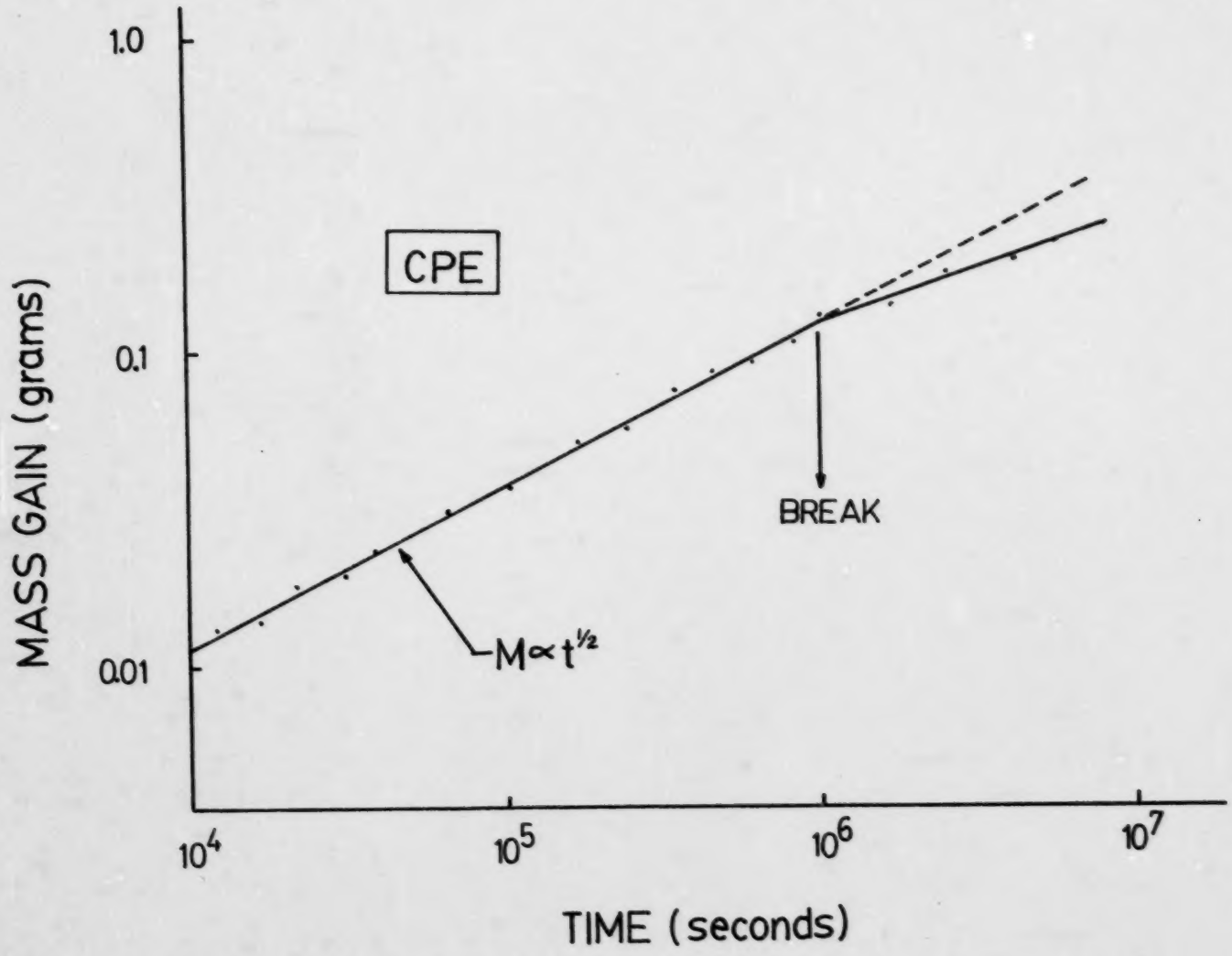


Figure 9 - Water Absorption Data for CPE at 30°C

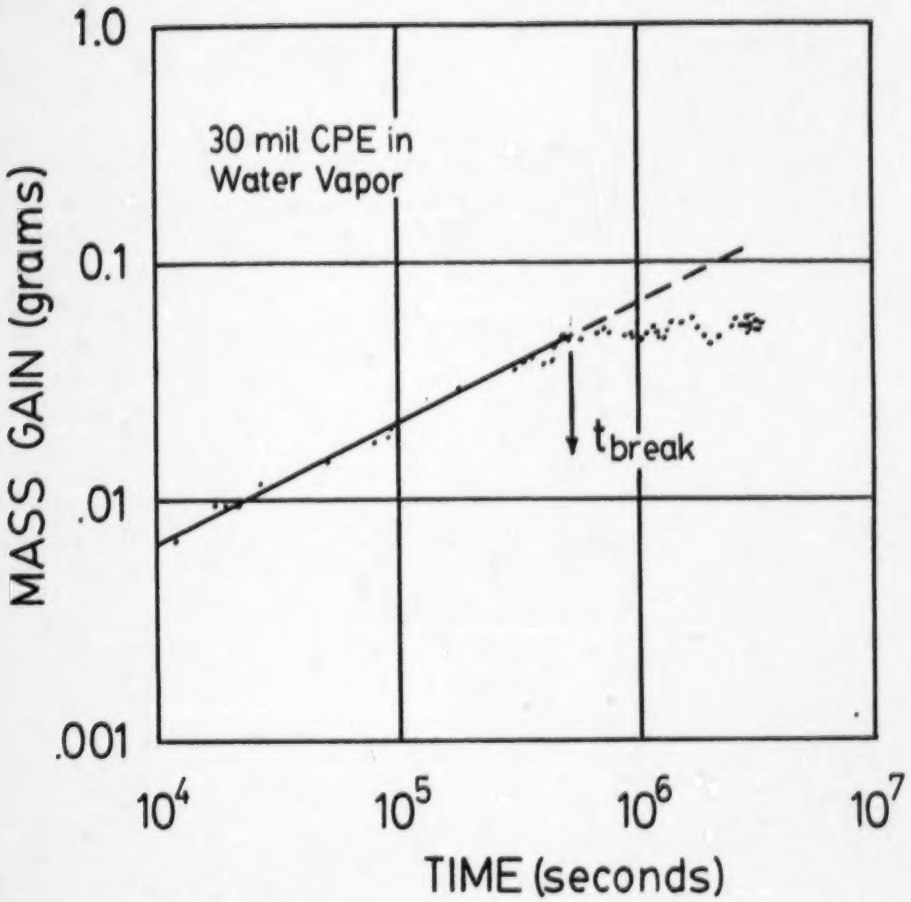


Figure 11 - Absorption Data of Water Vapor in 30 mil CPE

$$D = \frac{(0.5)^2 (.038)^2}{7 \times 10^5}$$

$$= 5.15 \times 10^{-10} \text{ cm}^2/\text{sec.}$$

However, this calculation is very suspect since the initial part of the curve does not follow the $t^{1/2}$ law. As with the liquid water absorption, there are large departures of the general results from simple diffusion theory, which makes the results somewhat suspect and of tenuous value. This will be discussed later.

RADIOACTIVE TRACER MEASUREMENTS TO DETERMINE THE DIFFUSION COEFFICIENTS (RT)

The diffusion coefficient of a particular molecule of a diffusant can be determined if part of the molecule (for example, a C-atom in benzene) can be made radioactive. The diffusion coefficient is determined by monitoring the radioactive disintegrations versus time at some convenient point. Water can be made radioactive (tritiated water), but it is hard to work with because the radioactive disintegrations produce β-rays (electrons) which are of very low energy and are very readily absorbed in any geomembrane (and even in air). Therefore, we are using more energetic β-emitters, namely benzene with carbon-14, even though water would be the preferred diffusant. Figure 12 shows a photograph and schematic diagram of the test device. The samples of FML are 8 cm in diameter and are clamped between two ground glass joints. It can be shown[23] that the solution for Fickian diffusion in a wide, thin sample is given by:

$$\frac{C_s - C}{C_s} = \frac{4}{\pi} \left[\exp\left(\frac{-D\pi^2 t}{4l^2}\right) \sin\frac{\pi x}{2l} + \frac{1}{3} \exp\left(\frac{-9D\pi^2 t}{4l^2}\right) \sin\frac{3\pi x}{2l} + \ldots \right] \qquad (2)$$

where

C_s = surface concentration at x = 0
C = concentration at position x in the geomembrane thickness (at time "t")
D = diffusion coefficient
t = time
l = thickness

For all but the very shortest of times, the first term in the series dominates, and the logarithm of both sides yields the following relationship;

$$\log\left(\frac{C_s - C_b}{C_s}\right) = \log\left(\frac{4}{\pi}\right) - \left(\frac{D\pi^2}{4l^2}\right) t$$

where C_b is the concentration of the diffusant at the far side, i.e. at x = l.

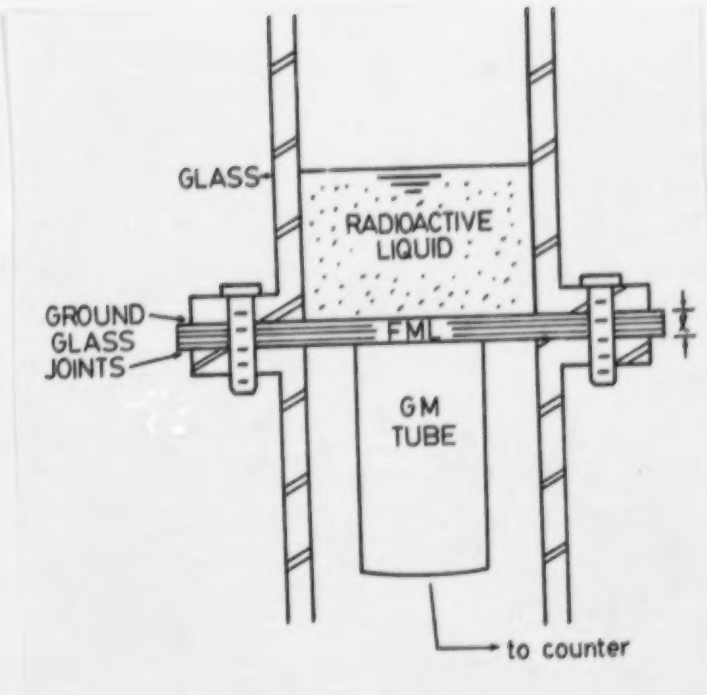


Figure 12 - Photograph and Schematic Diagram of the Apparatus for Determining the Diffusion Coefficient Using Radioactive Tracers

Figure 13 shows a schematic diagram where all the terms introduced in Equation 2 above are given pictorially. The concentration at the bottom of the FML, C_b, is proportional to the count rate measured at the bottom. This applies because any β-rays (electrons) reaching the counter at the bottom must have originated from nuclear disintegrations within a few mils of the bottom. The range of C^{14} β-particles in the FML's is only about 6 mils (0.006"). Thus for the GM tube to receive a count, a benzene molecule with C^{14} which had not yet disintegrated must have diffused from the top of the sample to essentially the bottom of the FML sheet.

The log C_s-C_b/C_s versus time gives a slope of $-D\pi^2/4l^2$, from which the value of D can be extracted. Figure 14 shows some "raw" radioactive data (counts/time vs. time) and Figure 15 shows the data put in the proper semilog form for analysis. Using this procedure a value of the benzene diffusion coefficient of 2×10^{-6} cm^2/sec is obtained for this particular geomembrane. The value of D can also be obtained from the time it takes the diffusing substance to travel from the top surface to the bottom surface (in "random jump" fashion). This is essentially the "time lag" needed for the data to start upward on Figure 14 or downward in Figure 15. The value of D can be arrived at from standard diffusion theory[25],

$$D = \frac{l^2}{2\Delta t} \qquad (3)$$

where Δt is the time lag shown on Figures 14 and 15, (about 36 minutes). This approach also gives $D = 2 \times 10^{-6}$ cm^2/sec.

This value is four orders of magnitude larger than that given for water diffusion in EPDM. It is known that benzene is a very good swelling agent for rubber-type materials[23] and swelling agents have unusually high values for apparent diffusion coefficients. This consideration, however hopefully does not diminish the value of the method because it is relative changes in diffusion properties with chemical exposure that are being sought in this project.

The reproducibility of the radioactive method can be seen in Table 5 where the D's determined by the time lag method are given for "identical" as received (control) samples. Subsequent "spot checks" on the chemically-exposed samples also showed this reproducibility.

Table 5 - Reproducibility of Radioactive Diffusion Data

FML	D(cm^2/sec)
EPDM	1.4×10^{-6}
	1.4×10^{-6}
	1.4×10^{-6}
PVC	1.3×10^{-6}
	1.3×10^{-6}
CPE	6.7×10^{-7}
	6.5×10^{-7}

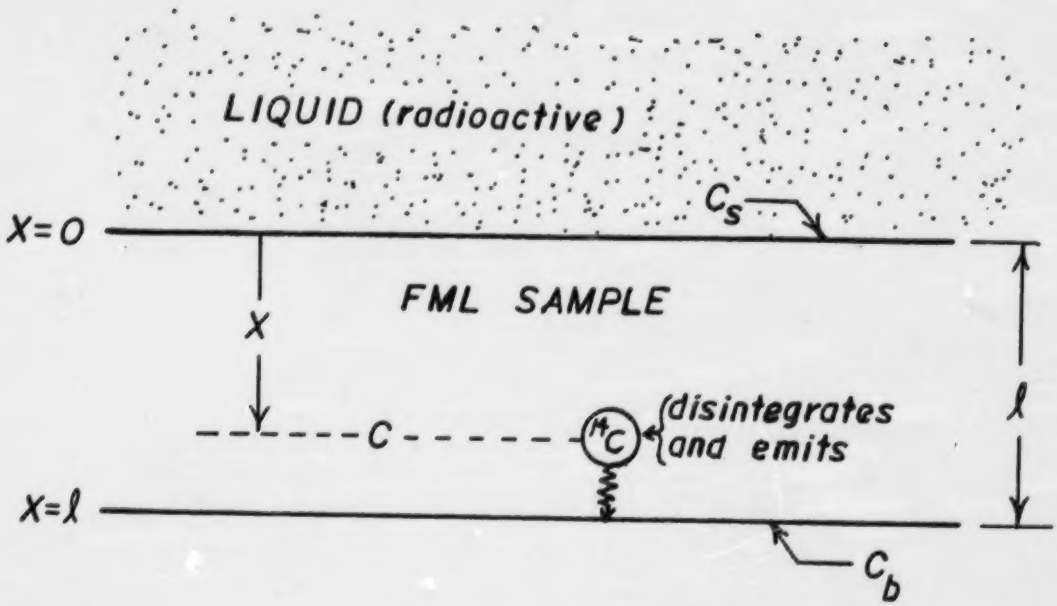


Figure 13 - Situation Involved for Diffusion of Radioactive Species from Top Surface

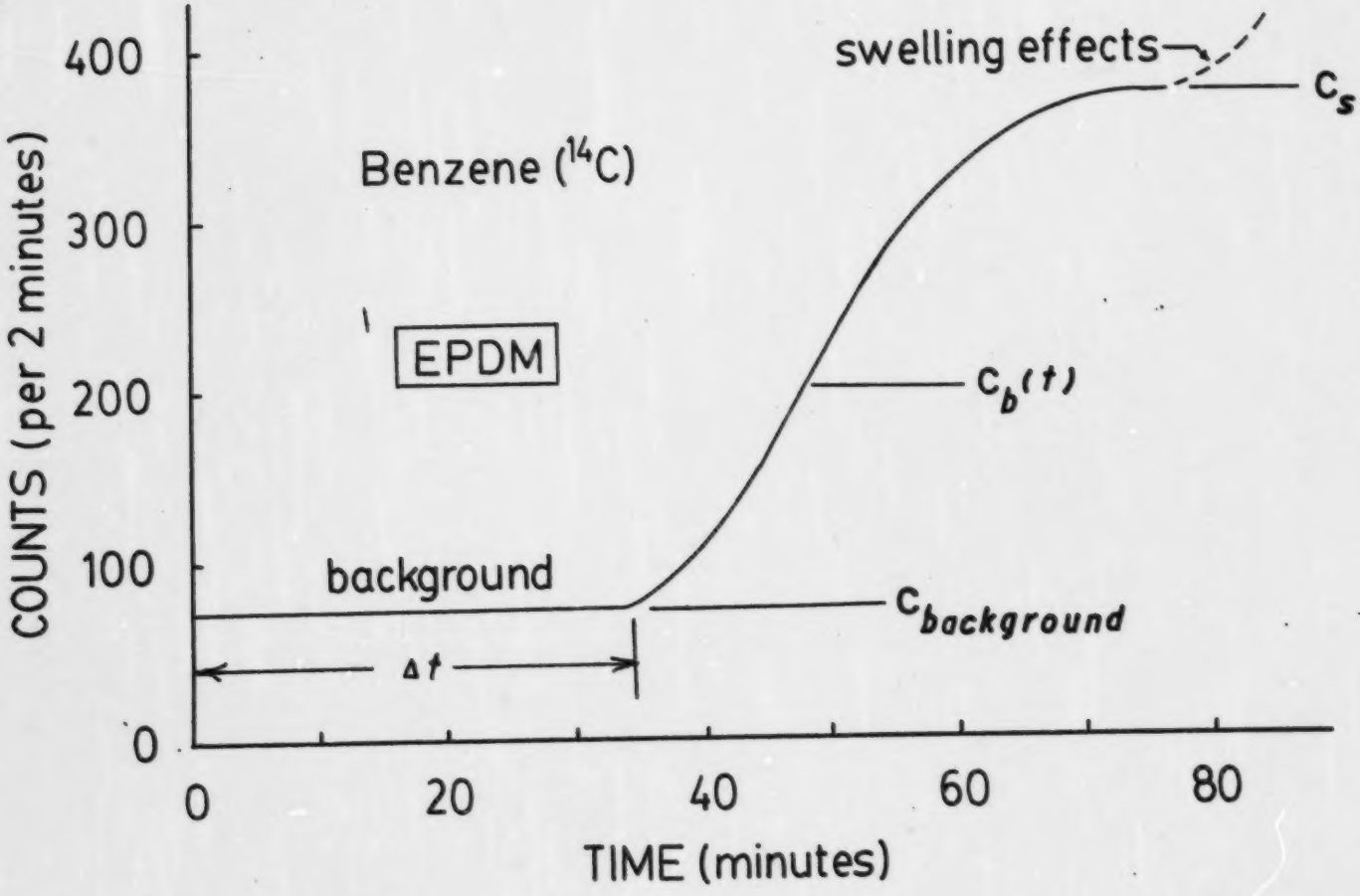


Figure 14 - Data for Diffusion of Radioactive Benzene (^{14}C) in EPDM

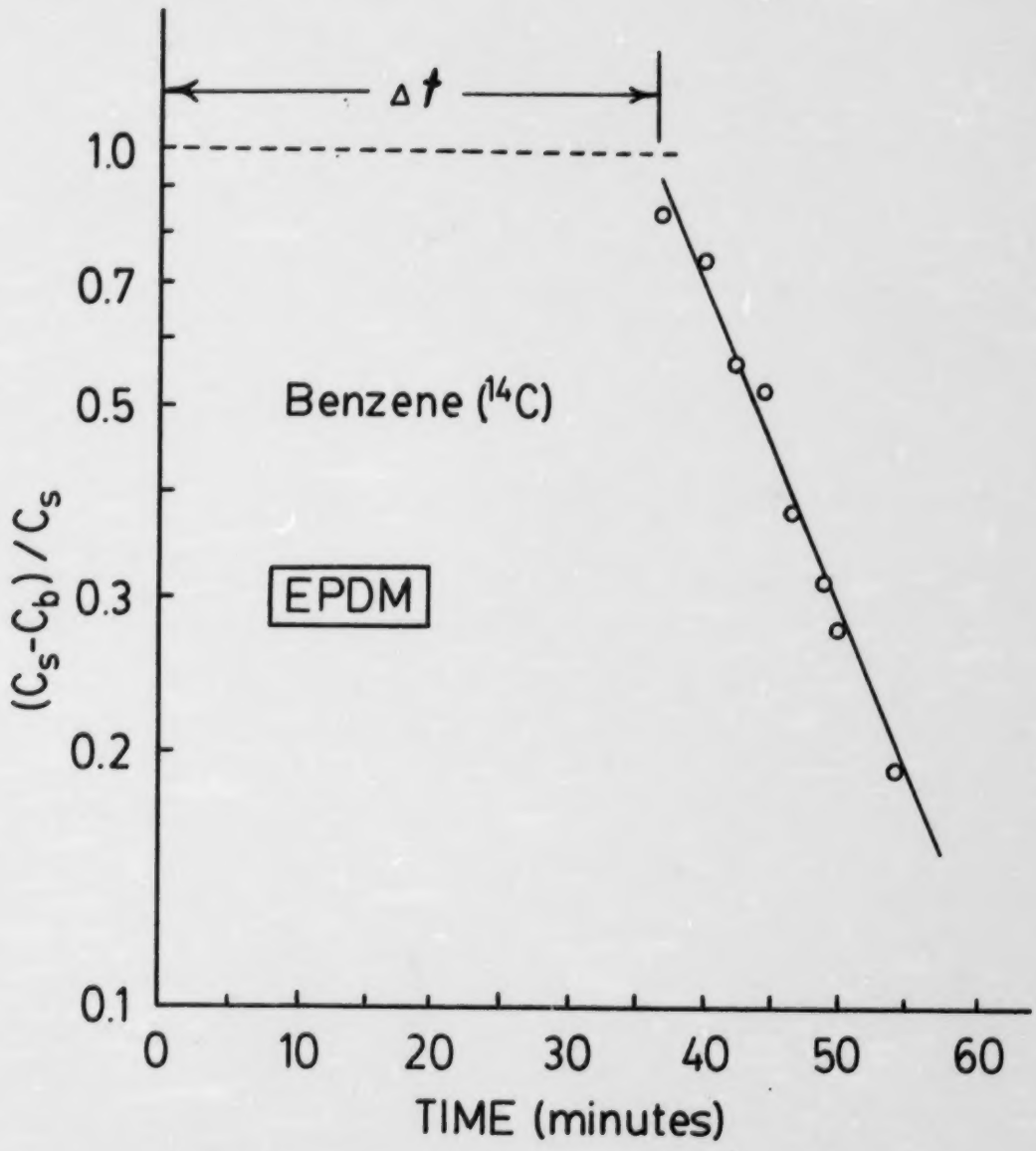


Figure 15 - Data Using Radioactive Tracers Illustrating Benzene (^{14}C) Diffusion Through EPDM

BENZENE ABSORPTION TO DETERMINE DIFFUSION COEFFICIENTS (BA)

For materials with low solubility of diffusant, a relatively large amount of radioactivity would be necessary to produce a high enough count rate to be usable with the simple Geiger-Mueller tube detection being used here. High density polyethylene (HDPE) is such a low solubility material. Therefore an alternate method (from radioactive tracer) was used with HDPE in order to avoid the higher levels of radioactivity. (The individual samples would need to have about 5μ Ci of activity versus the 0.1μ Ci used in the PVC, EPDM and CPE samples. This is still very far below a dangerous level, however.)

The liquid (benzene) absorption method was used as the alternative, and the theory is given in the liquid water absorption section (Equation 1).

MICROSTRUCTURAL OBSERVATIONS

Some preliminary work was performed in trying to see if severe chemical attack could be monitored on a very small scale using the scanning electron microscope (SEM). Standard SEM procedures were utilized with a JEOL-SEM. Observations were made of the as-received and severely-chemically attacked FML's. Surface and transverse (cut and cyrofractured) sections were observed. The FML used was PVC and the chemical agent was methylene chloride, which is extremely corrosive toward PVC. The results were not promising at all. Gross chemical attack, which could be seen very easily with the naked eye, was not accompanied by characteristic crack or craze patterns (or the like) in the SEM observations. For completeness, however, a few SEM photos will be presented in the Results Section.

DIFFERENTIAL SCANNING CALORIMETRY MEASUREMENTS

Standard differential scanning calorimeter (DSC) measurements were made (using a Dupont Thermal Analyzer) on selected as-received and treated FML materials, to ascertain if a chemically-induced structural change could be detected with this method. There is very little if any data in this regard in FML's in the open literature. Some data will be presented in the Results Section.

SECTION 6
RESULTS OF MASS TRANSPORT MEASUREMENTS ON SAMPLES EXPOSED TO VARIOUS CHEMICALS

The results will be presented in two sets. The first set will be the results from Phase I, which had chemical exposure times for up to six months. The second set will be from Phase II, which had exposure times up to 15 months. The new set included a new FML and a new chemical to make the study more representative and complete. The two sets of data cannot be presented together for reproducibility is not good when starting with different lots of the "same" FML.

PHASE I (UP TO SIX MONTHS EXPOSURE)

Water Vapor Transmision Results

The results of chemical exposure are shown in Figures 16, 17 and 18. Duplicate samples were run in all cases. In Figure 16, it is seen that the NaOH and H_2SO_4 solutions (10%) have very little effect on the WVT of PVC, even for periods of one half year. On the other hand, the chemicals which "leach" the plasticizer from PVC, namely phenol and xylene, produce a very definite lowering of the WVT. PVC is very stiff after exposure to these latter two chemicals, and it is very well known in the polymer field that if a material becomes stiffer, the transport properties almost always decrease in magnitude.

Figure 17 shows that the WVT in EPDM is affected very little by 6 months exposure to the four chemicals.

Figure 18 shows that the WVT in CPE is affected very little by acids and bases, but significantly increases upon exposure to phenol. PVC is completely destroyed by xylene in about a day, so no WVT results are shown for CPE in xylene.

Thus it is seen that the WVT can be significantly reduced (Fig. 16), remain the same (Fig. 17) or increase significantly (Fig. 18) upon chemical exposure. The most interesting result would seem to be the effect of phenol on CPE, for if the WVT trend continues upward, eventually a time will be reached where the WVT would be unacceptably high for field use. (Refer to Figure 1.) This "lifetime" would probably have to be an extrapolated value.

Water Absorption and Water Vapor Absorption

There are very significant problems in determining the diffusion coefficients in FML's via water absorption or water vapor absorption. The main problem with liquid water absorption is that in many cases the FML does not achieve a constant (equilibrium) weight during a very long immersion time. Figure 19 shows the CPE has not achieved an equilibrium weight in over 100 days. Many samples were monitored for 200 days with no equilibrium weight achieved. The diffusion coefficient cannot be determined without this final weight. In spite of this serious problem, many samples showed very nearly the expected (Fickian $t^{1/2}$ power law in the initial stages of absorption. (Refer to Figure 19.) Obviously the entire uptake process is more complicated than simple diffusion, and may be complicated by surface adsorption effects.

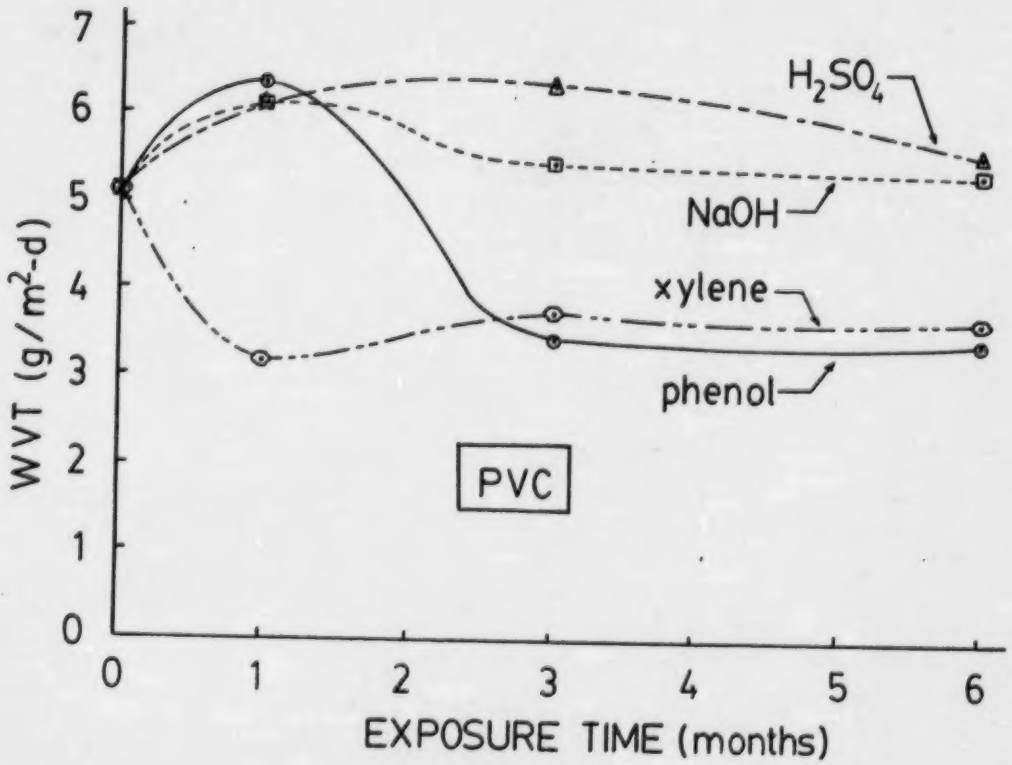


Figure 16 - WVT Results for PVC as a Function of Exposure Time to Various Chemicals

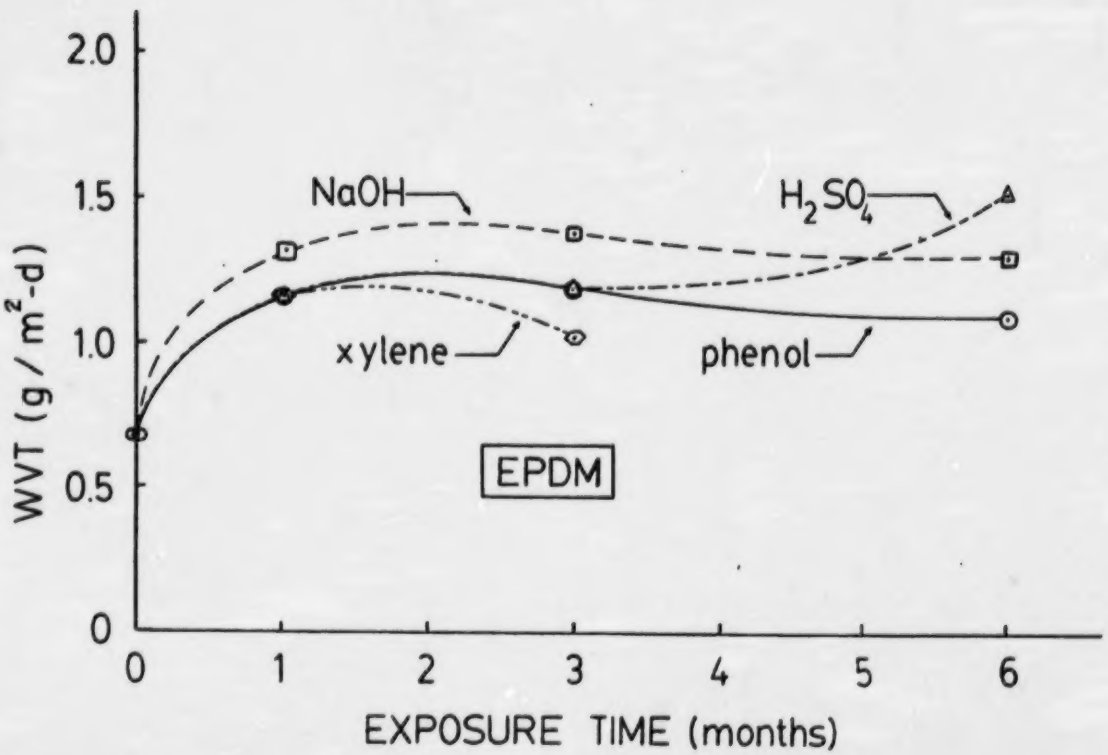


Figure 17 - WVT Results for EPDM as a Function of Exposure Time to Various Chemicals

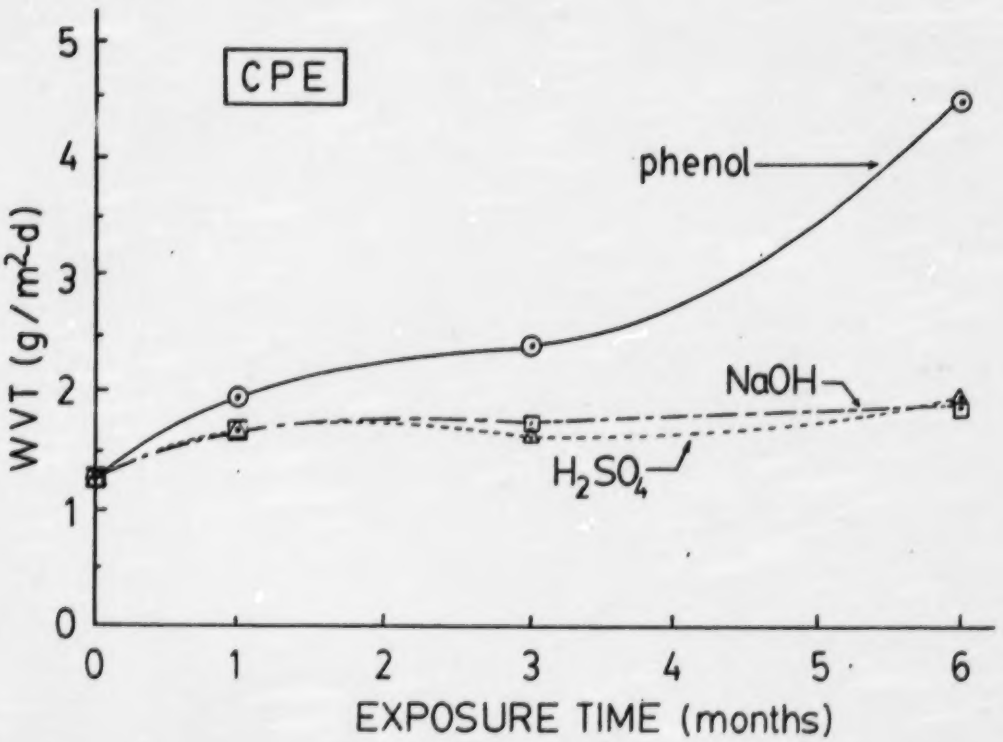


Figure 18 - WVT Results for CPE as a Function of Exposure Time to Various Chemicals

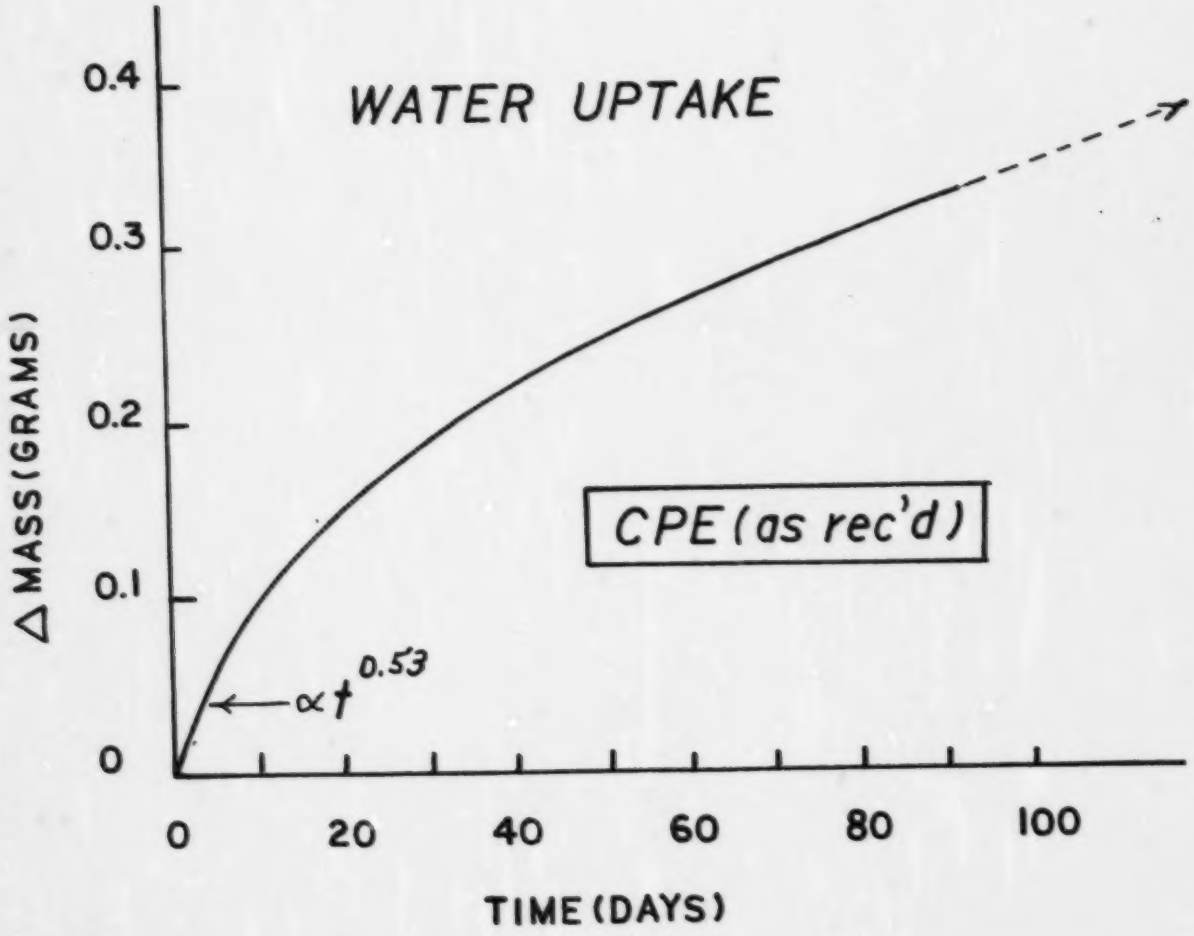


Figure 19 - Water Uptake as a Function of Time for CPE Immersed in Water (As-received condition)

In the case of water vapor absorption, the main problem is the lack of an initial $t^{1/2}$ time dependence*, even though a constant weight is achieved in a reasonably time. The uptake is not simple Fickian and hence extraction of a D-value from the data is extremely suspect. Figure 20 shows such a case with EPDM.

There are other problems in this measurement technique:

- PVC absorbs a very small amount of water, making analysis next-to-impossible.
- Some samples actually lose weight while in contact with water, indicating some of the chemical gained during exposure is still coming out of the FML (in spite of the vacuum dessication before measurement).
- In many cases the data is scattered and shows no definite trends.

The bottom line is that water and water vapor absorption are not reliable methods with which to determine the diffusion coefficient of water in commercial FML's. Some others[26,27,28] who have worked in this area have the same type of results as those found here, however their conclusions were not as negative as the present authors feel is warranted.

On the positive side, in the limited number of cases where the method does work, it shows diffusion coefficients consistently in the 10^{-9} cm^2/sec range for both the thermoplastic (CPE and PVC) and thermoset (EPDM) types. (See Table 6.) However the methods are not reliable enough to follow the degradation of FML's due to chemical exposure. There are simply too many problems with the technique as applied to these commercial materials. The results given in Table 6 were obtained (for as-received materials), in a separate study, by immersing the FML in the indicated liquid (at 30°C) and determining the weight gain as a function of time. The results are only given if the initial time exponent is near 1/2, and a reasonably constant final weight was achieved. These values should only be considered accurate to within an order of magnitude, due to all the problems with the absorption methods previously noted.

For completeness (and possible future use to determine the actual mechanism of the total absorption process), Appendix B contains a concise presentation of all the data obtained by the water and water vapor absorption methods. Appendix B contains D-values where possible (control and exposed), weight gained in 20 days, and the initial time-dependence exponent for all three FML's.

Radioactive Tracer Measurements

Figures 21, 22 and 23 shows the results of the diffusion coefficient for benzene as a function of chemical exposure. The results of PVC (Fig. 21) are in general agreement with those found in the WVT work in PVC (Fig. 16). The exposure to acid and base do little to the diffusion coefficient, whereas the leaching agents, phenol and xylene lower the diffusion rate as the plasticizer is "leached-out" and the PVC becomes stiffer.

---

*This lack of a $t^{1/2}$ dependence as well as equilibrium not being achieved in any reasonable time has also been seen frequently by the few other workers in this field (26,27,28).

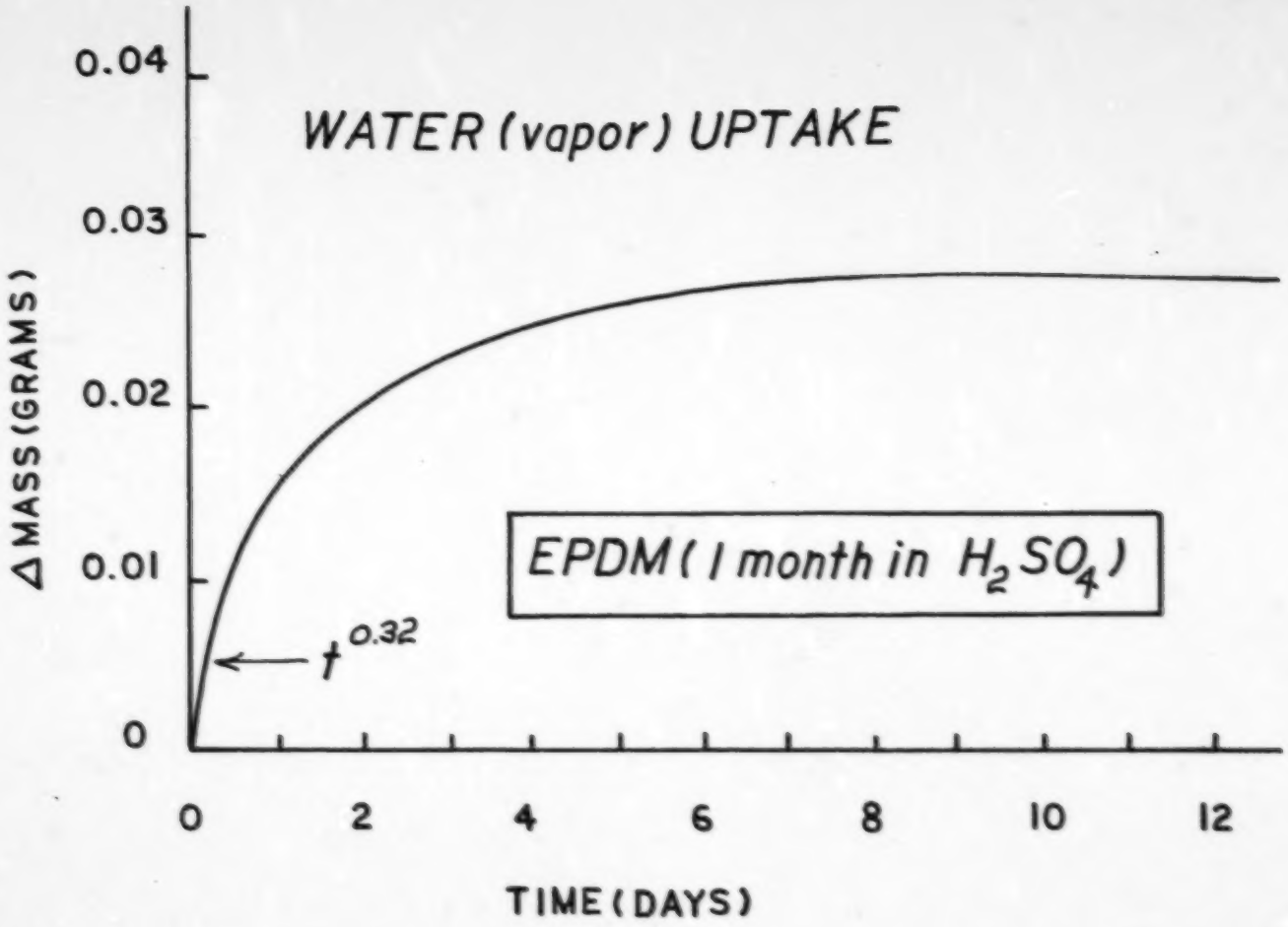


Figure 20 - Water Vapor Uptake as a Function of Time for EPDM (Exposed to 10% H_2SO_4 for one month).

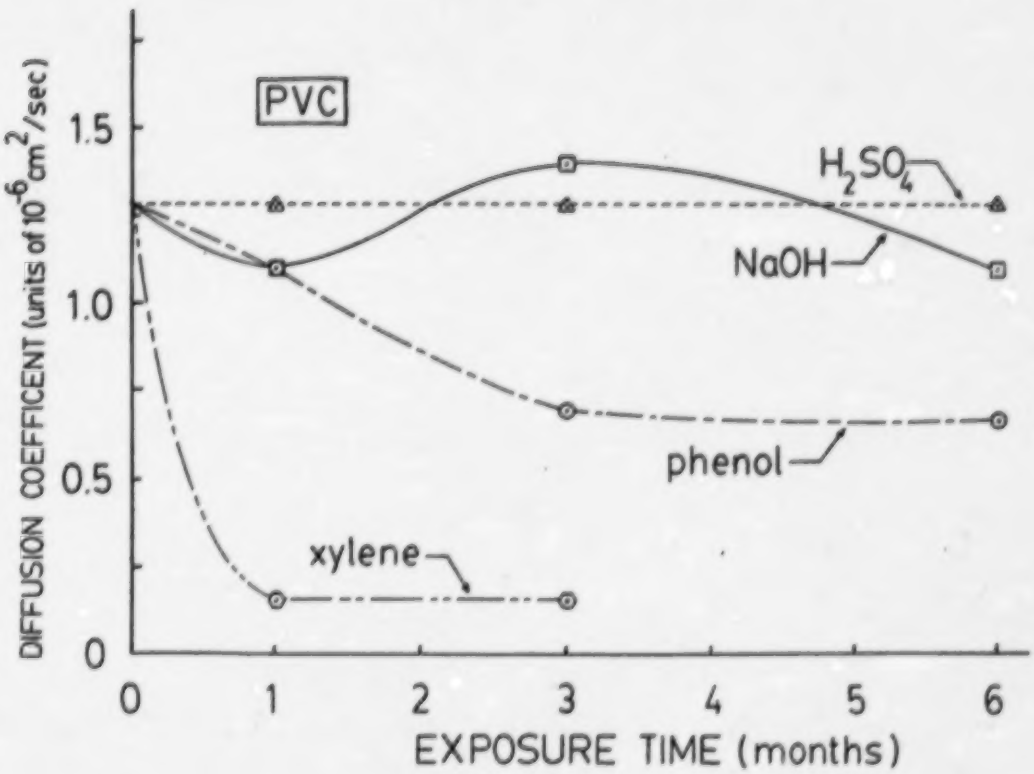


Figure 21 - Diffusion Coefficient of Radioactively Tagged Benzene (^{14}C) in PVC as a Function of Exposure Time to Various Chemicals

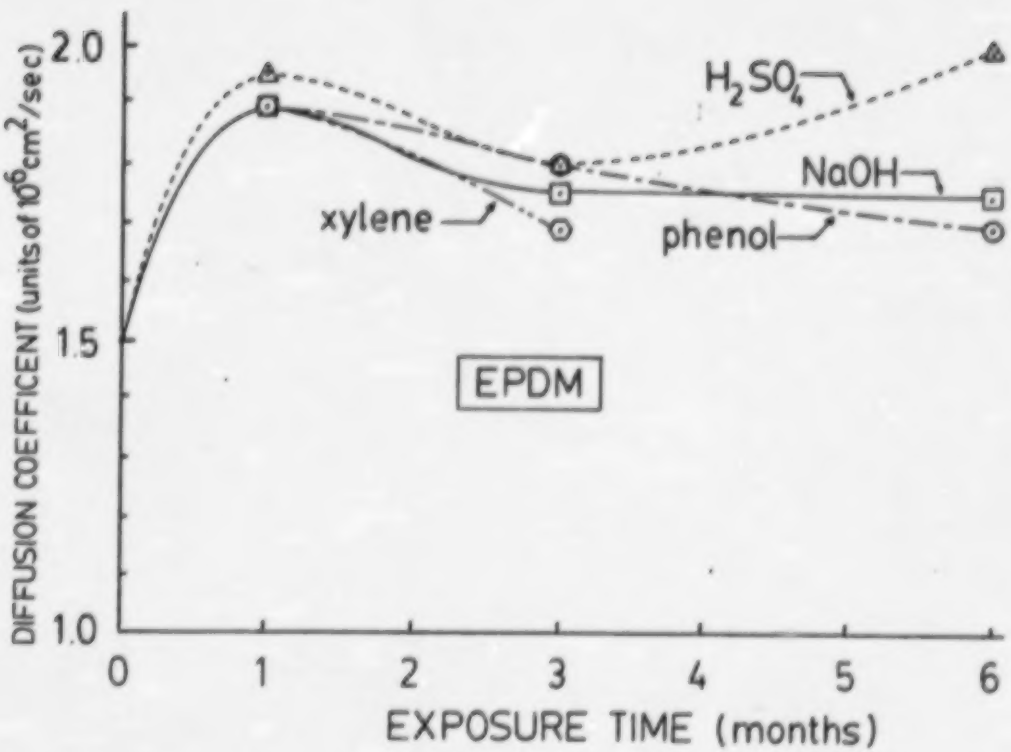


Figure 22 - Diffusion Coefficient of Radioactively Tagged Benzene (^{14}C) in EPDM as a Function of Exposure Time to Various Chemicals

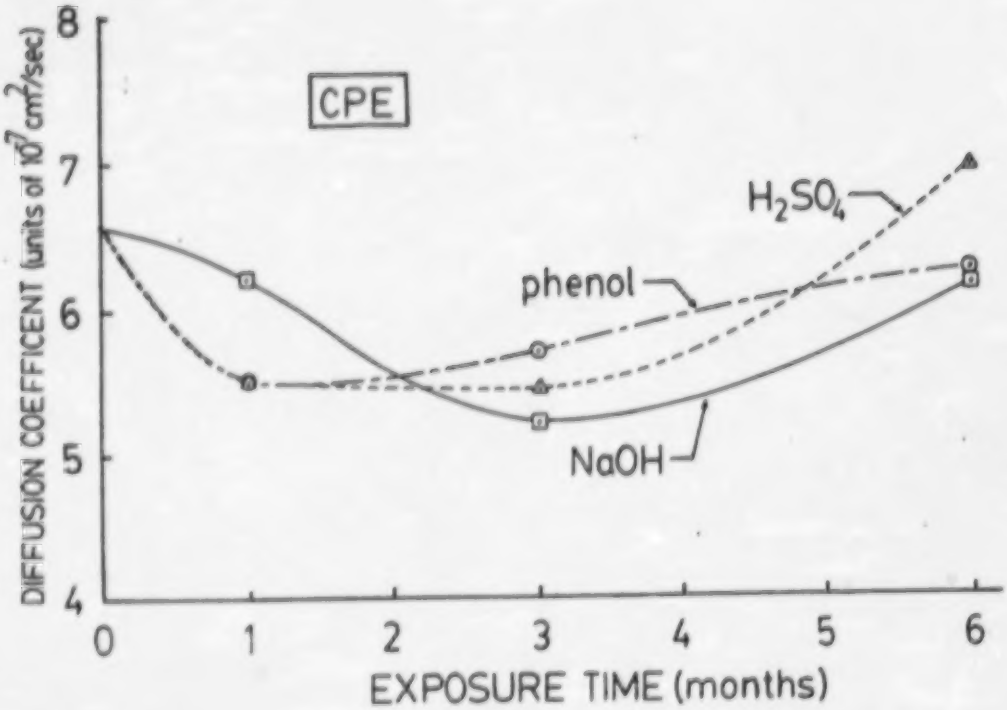


Figure 23 - Diffusion Coefficient of Radioactively Tagged Benzene (^{14}C) in CPE as a Function of Exposure Time to Various Chemicals

Table 6 - Diffusion Coefficients (in cm^2/sec) Found in This Study

	CPE	EPDM	PVC
Water	0.3×10^{-9}	0.9×10^{-9}	*
10% NaOH	1.1×10^{-9}	1.2×10^{-9}	*
10% H_2SO_4	8.2×10^{-9}	1.0×10^{-9}	*
10% Phenol	4.0×10^{-9}	0.16×10^{-9}	0.21×10^{-9}
Xylene	+	+	+
3% Salt Water	0.3×10^{-9}	1.6×10^{-9}	1.6×10^{-9}
10% Acetone	*	1.0×10^{-9}	*
50% Acetone	*	1.0×20^{-9}	*

*Values not obtained because weight gain was either too slow or too fast.
+Reached equilibrium before first data point was taken.

The results for EPDM (Fig. 22) are in exact agreement (with respect to relative changes) with those given in WVT (Fig. 17). This agreement between the two methods for PVC and EPDM is very encouraging, but unfortunately does not seem to carry over completely to CPE, for the six month exposure work.

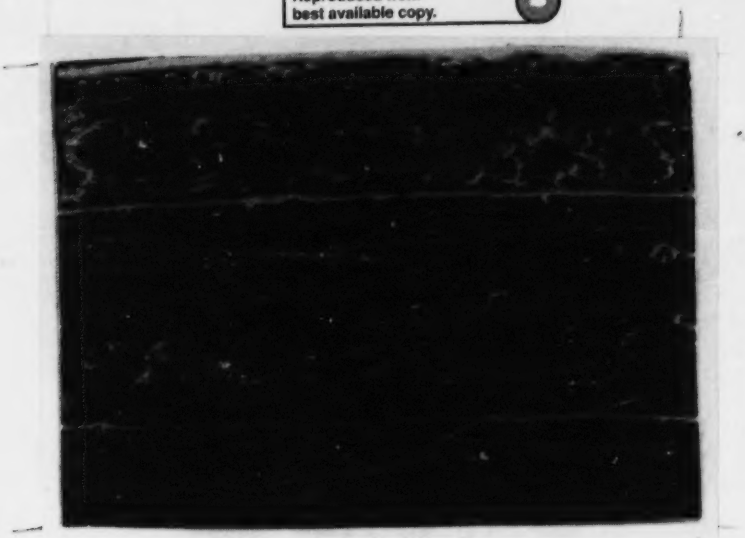
The CPE diffusion results as a function of chemical exposure, are shown in Figure 23. Agreement with the WVT results for CPE (Fig. 18) is good for the acid and base, but is poor for phenol. Whereas the WVT results showed CPE to become quite a bit more permeable (~ four times) after 6 months exposure to phenol, the benzene diffusion shows no increase after 6 month's exposure to phenol. (Recall the xylene "destroyed" CPE in a few days - so no results are given.) This is quite an important (and somewhat discouraging) result, for the CPE/phenol situation appeared from the WVT to be a prime candidate for FML lifetime prediction via transport measurements. Further work in this regard will be discussed in the next section which involves longer chemical exposure times of the FML's.

Microstructural Observations

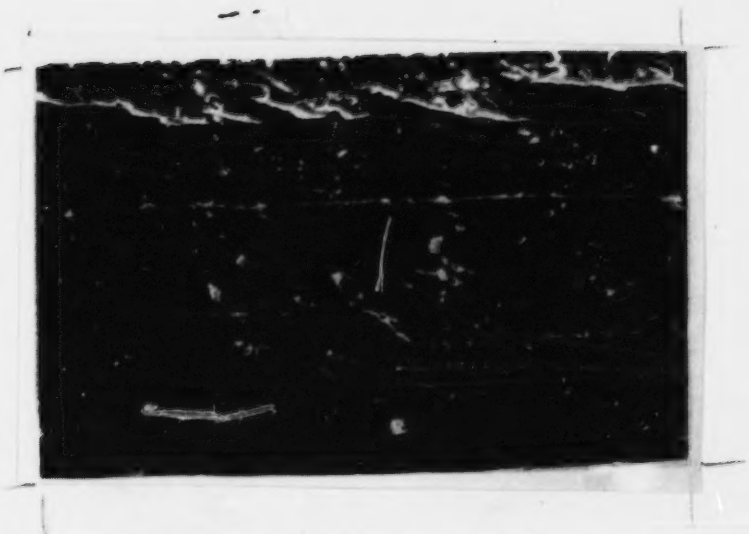
Presented here are some SEM results of PVC severely attacked by methylene chloride. Figure 24 shows transverse sections through an as-received sample and a sample soaked for four minutes in methylene chloride. The magnification is 100 times. The sample soaked for four minutes was quite strongly attacked (via visual observation of physical integrity), however the SEM observations give no clear-cut indication of damage - there are no developed cracks or crazes, or other signs of damage. The only difference is the position of the plys, and this is probably due to the two photographs representing different samples (even though taken from the same roll of FML).

Surface views are shown (Figure 25) at 300 times magnification for one minute and three minute soak times. The longer exposure time produced much more visual damage, but again there are not clear indications of damage from the SEM photos.

Reproduced from
best available copy.

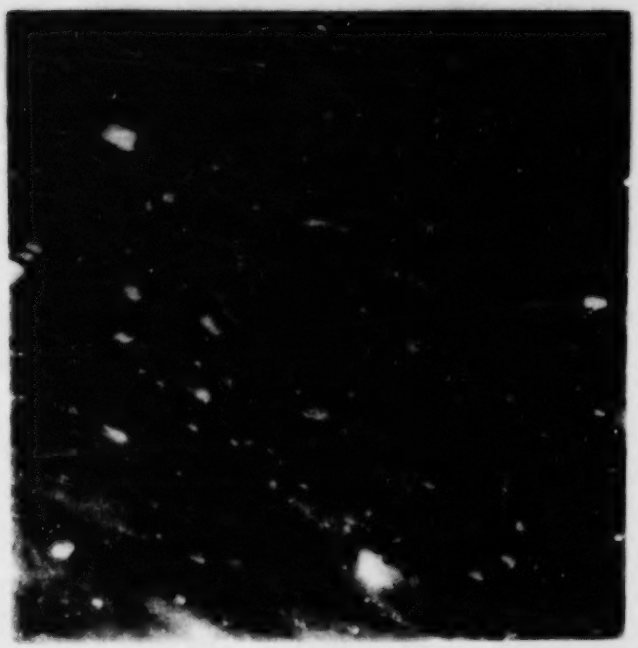


a) As Received



b) Soaked 4 Minutes in Methylene

Figure 24 - SEM Photographs of PVC - 100X Magnification of Transverse Section



a) Soaked 1 Minute in Methylene Chloride

b) Soaked 3 Minutes in Methylene Chloride

Figure 25 - SEM Photographs of PVC - 300X Magnification of Surface Section

Figure 26 shows surface views at 3000 times magnification for three and ten minute soak times. In this case the ten minute material is no longer in one piece (severely damaged), yet the SEM photos indicate no change.

Even though our microstructural observation studies were quite preliminary, they were of such a negative nature, that further work in this area was halted in favor of the mass transport measurements.

Differential Scanning Calorimeter Results

Figure 27 shows the DSC traces for PVC treated with xylene.* Xylene removes plasticizer and this is very vividly seen in the DSC traces. The as-received material has a faint indication of a glass transition at -45°C. After exposure to xylene for one month, a very well-defined glass transition occurs at about 30°. Exposure of three and six months results in the same transition temperature. Evidently, after one month exposure to xylene, PVC loses very little more plasticizer. After one month exposure the material is noticeably stiffer.

Figure 28 shows the DSC results for CPE exposure to phenol. The as-received material has some minor structure between -36° and 26°C and between +35° and +55°C. Subsequent structure become evident as the CPE is exposed to phenol for one month, three months and six months. The longer the exposure, the more the structure in the DSC trace. Exposure to phenol has "freed-up" the structures above -26°C so that they can move and absorb heat. Even though a great variety of thermal effects are evidenced in the DSC work, there was no significant stiffening (or softening) of the structure.**

Table 7 summarizes the work of Phase I. The total change in transport property from zero months to six months is given for each FML/chemical combination. Also given is the trend in transport property at six months, i.e., whether it is increasing, decreasing or steady. The arbitrary (but one which the authors feel is reasonable) criteria for a degrading effect, due to a particular chemical exposure, is a large absolute increase and a continuing upward trend at 6 months.

Table 7 shows that only CPE exposed to phenol and EPDM exposed to H_2SO_4 give a definite indication of damage from the transport measurements. (Unfortunately the EPDM work in H_2SO_4 was not continued to longer exposure times in Phase II, to be discussed.)

PHASE II (UP TO FIFTEEN MONTH EXPOSURE)

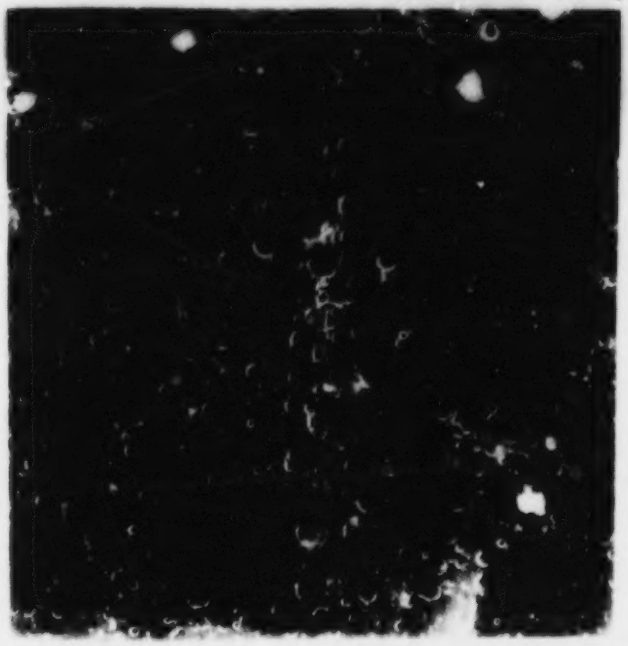
As a result of the work of Phase I it was decided to extend some of the previous testing to 15 months exposure and also include some new elements in

---

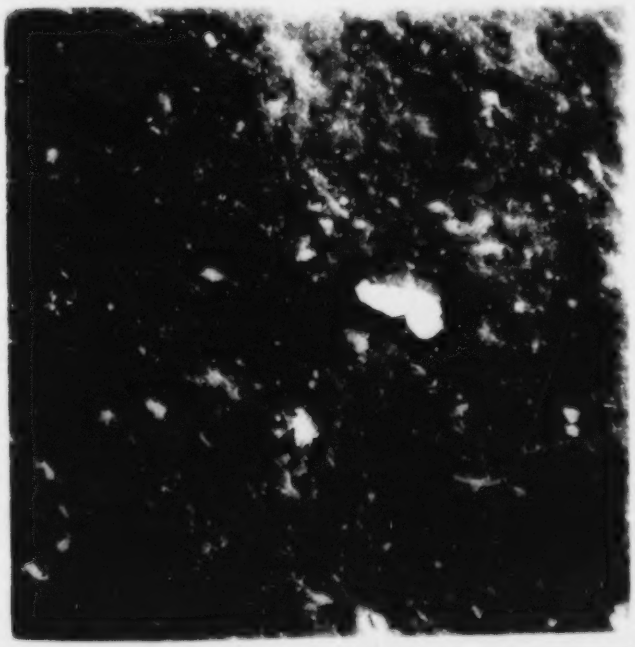
*These curves are redrawn from the original graphs. The "raw" experimental data is shown in Appendix C.

**It would be important to prove that the additional thermal structure seen in Figure 28 is not due to the phenol itself. However it is difficult to imagine that a compound as relatively simple as phenol could produce the myriad number of thermal effects observed.

Reproduced from
best available copy.



a) Soaked 3 Minutes in Methylene Chloride



b) Soaked 10 Minutes in Methylene Chloride

Figure 26 - SEM Photographs of PVC - 3000X Magnification of Surface Section

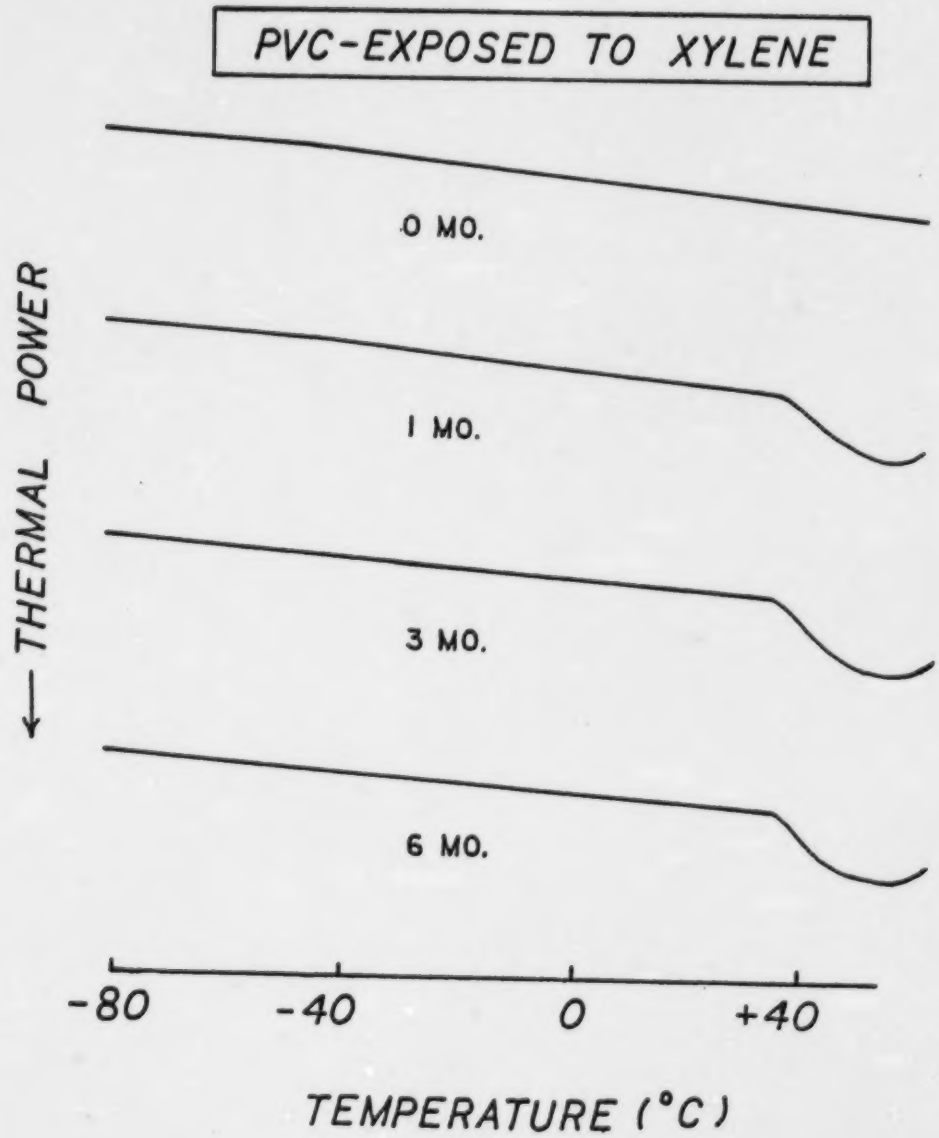


Figure 27 - Differential Scanning Calorimetry (DSC) Results for PVC as a Function of Exposure Time to Xylene. The ordinate represents the thermal power supplied to the sample to keep a constant temperature rise rate. The abscissa is the temperature of measurement. If the thermal power rises (downward trend) then additional heat is needed in this temperature range to "excite" (activate) additional modes of motion of the solid sample.

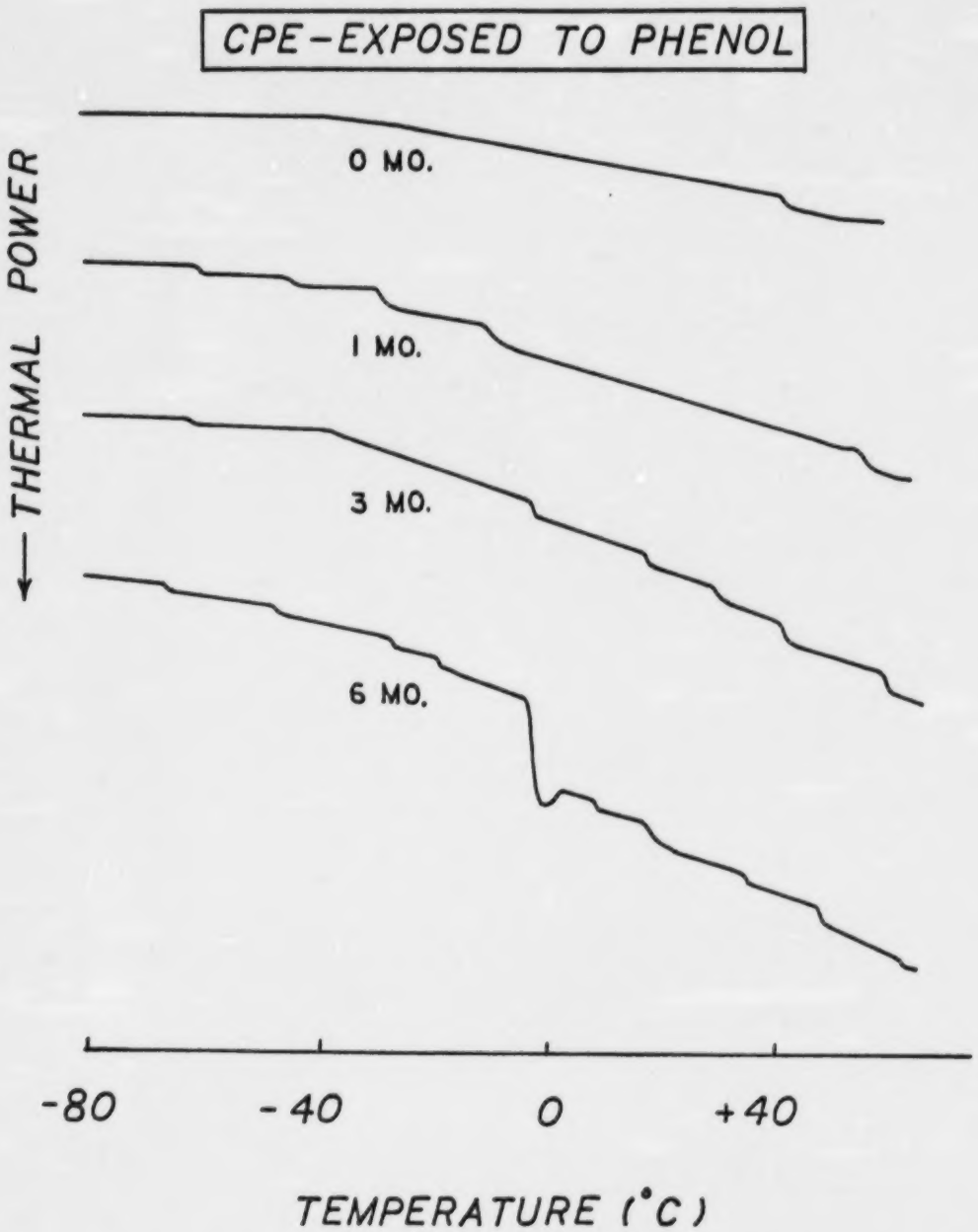


Figure 28 - Differential Scanning Calorimetry (DSC) results for CPE as a Function of Exposure Time to Phenol. The ordinate represents the thermal power supplied to the sample to keep a constant temperature rise rate. The abscissa is the temperature of measurement. If the thermal power rises (downward trend) then additional heat is needed in this temperature range to "excite" (activate) additional modes of motion of the solid sample.

Table 7 - Summary of the WVT and RT Results for 6 Month Exposure

	6 Month's Exposure	
PVC	WVT	RT
H_2SO_4	+ 12% - steady	+ 4% - steady
NaOH	+ 10% - steady	-11% - steady
Phenol	- 30% - steady	-50% - steady
Xylene	- 25% - steady	-85% - steady
EPDM		
H_2SO_4	+138% - rising	+37% - rising
NaOH	+100% - steady	+20% - steady
Phenol	+ 70% - steady	+17% - steady
Xylene	-	-
CPE		
H_2SO_4	+ 54% - steady	+15% - rising
NaOH	+ 46% - steady	-11% - steady
Phenol	+260% - rising	- 9% - steady
Xylene	-	-

- First term is the change from as-received to the 6 month exposure value, e.g., 12%..
- Second term is the trend of the data at the 6 month mark, e.g., steady.

the exposure matrix. The matrix for Phase II was:

- high density polyethylene (HDPE) - water, NaOH, H_2SO_4, phenol and xylene
- chlorinated polyethylene (CPE) - water, NaOH, H_2SO_4, and phenol
- water exposure - EPDM, PVC, CPE and HDPE

The exposure was one sided in tubs as in Phase I and WVT and RT measurements were made on all samples, except the HDPE where benzene absorption replaced RT, for reasons discussed earlier. (See pages 11 and 14 for the exposure matrix of Phase I.)

Water Vapor Transmission Results

Figure 29 shows the results for CPE with various chemical exposures. There is a general lowering of WVT with exposure time for NAOH, H_2SO_4 and water. However there is a marked increase in WVT with exposure to phenol. This marked increase was also observed in Phase I (up to 6 months exposure).

Figure 30 shows the results for water exposure of the four FML's. The water does not affect the WVT of any of the material. Note the large difference in values of the WVT for the various FML's, with the results for HDPE at least an order of magnitude lower than any of the others.

Figure 31 indicates the results of exposure of HDPE to the various chemicals. There is essentially no change due to any of the chemicals for up to 15 months exposure. It should be mentioned here as indicated in Section 5.2, that 0.10 g/m^2-day is the minimum possible value that can be measured in this study. Therefore if the value dropped below this value, there would be no means of measuring it in the present study.

Radioactive Tracer and Benzene Absorption Results

Figure 32 shows the results of RT measurements for CPE with exposure to the various chemicals for up to 15 months. All chemicals produce an initial increase in the diffusion coefficient from 4 to 7 x 10^{-7} cm^2/sec for one month exposure. Thereafter the diffusion coefficient decreases very slightly for NaOH, H_2SO_4 and water, but continues to increase for phenol exposure. This mimics the trends in the WVT results, although the relative increase and decrease are larger in the case of WVT.

Figure 33 shows the results for the various FML's in water. As in the case of WVT, there is little effect on the diffusion coefficient with exposure to water. HDPE still has a diffusion coefficient which is about an order or magnitude less than the other three FML's. The diffusion of benzene in PVC is not so rapid (relative to the other FML's) as it was for the WVT. (See Figure 30).

Figure 34 indicates the diffusion coefficient in HDPE as influenced by exposure to the various chemicals. Again, as in the WVT tests, little effect of chemical exposure is present.

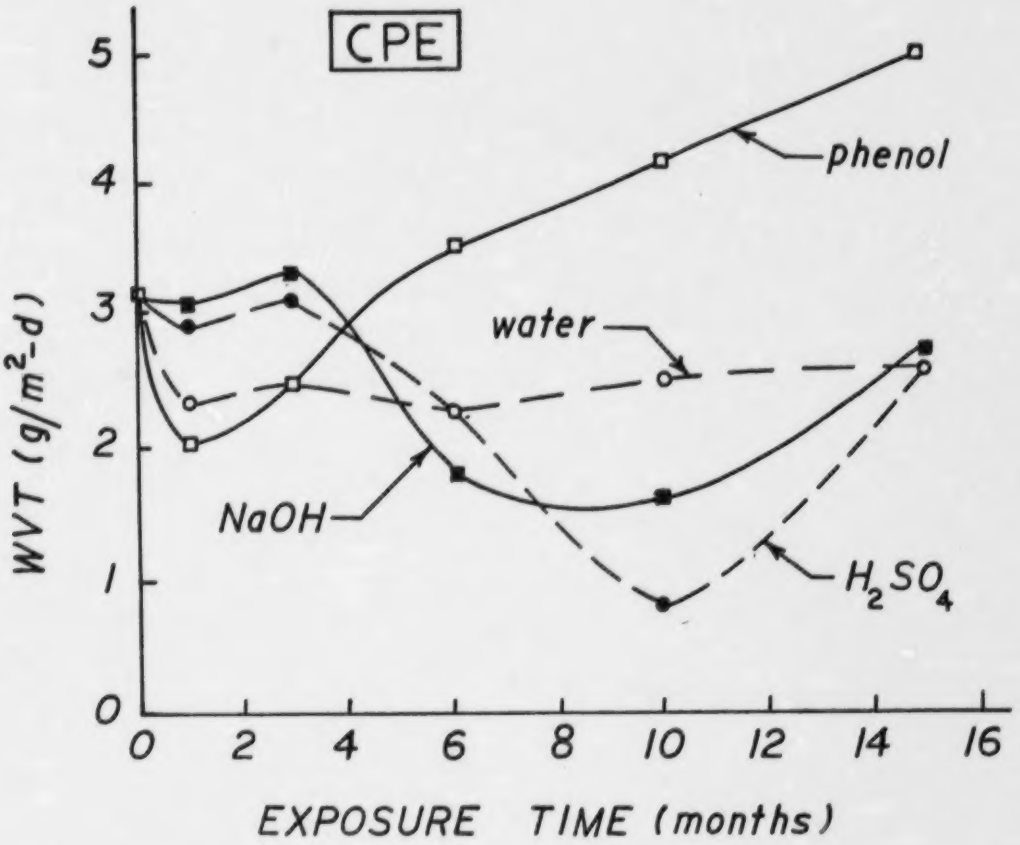


Figure 29 - WVT Results as a Function of Chemical Exposure Time for CPE (15 month exposure)

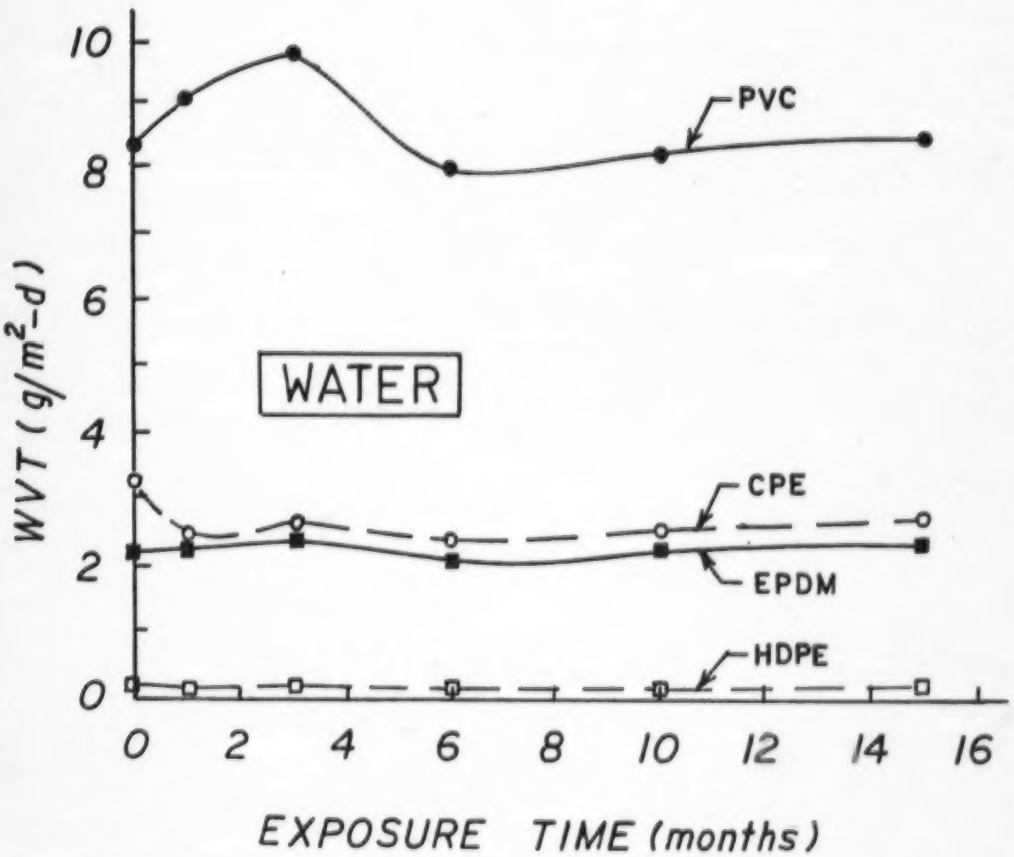


Figure 30 - WVT Results for Various FML's as a Function of Water Exposure Time (15 month exposure)

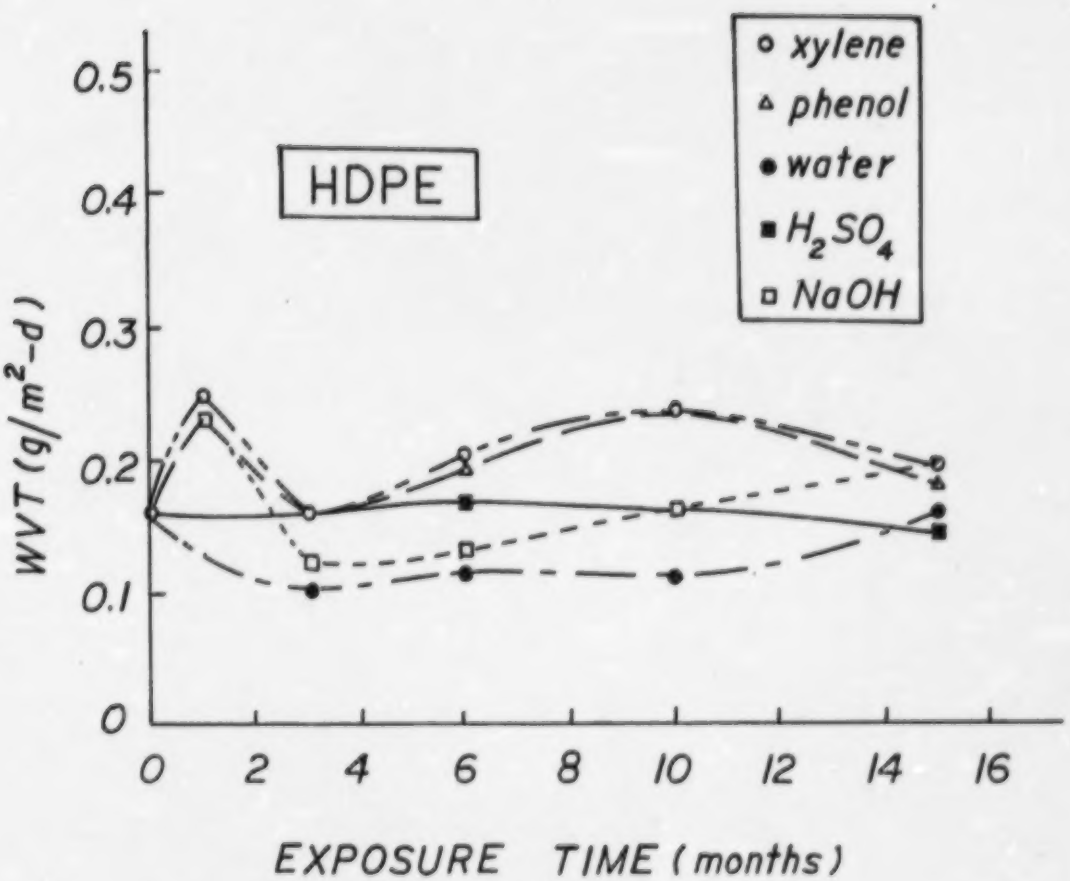


Figure 31 - WVT Results as a Function of Chemical Exposure Time for HDPE (15 month exposure)

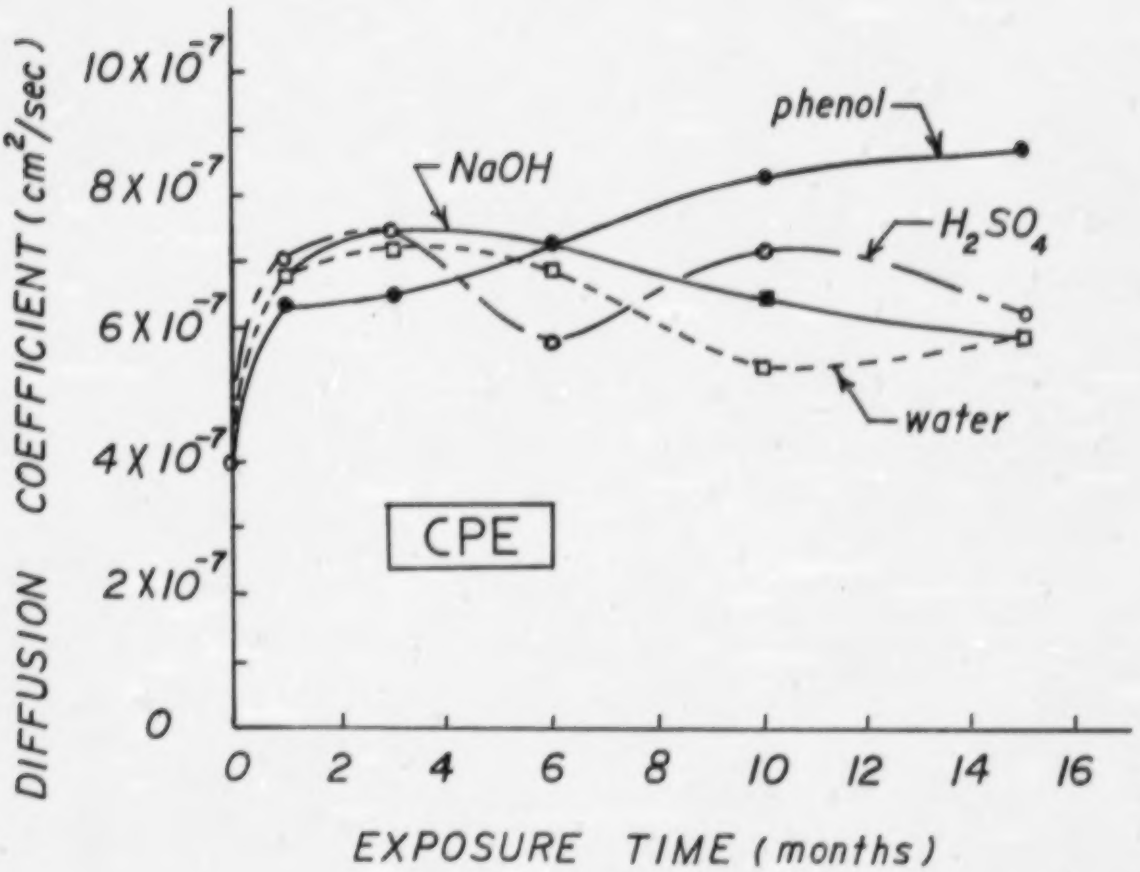


Figure 32 - Diffusion Coefficient Results as a Function of Chemical Exposure Time for CPE (15 month exposure)

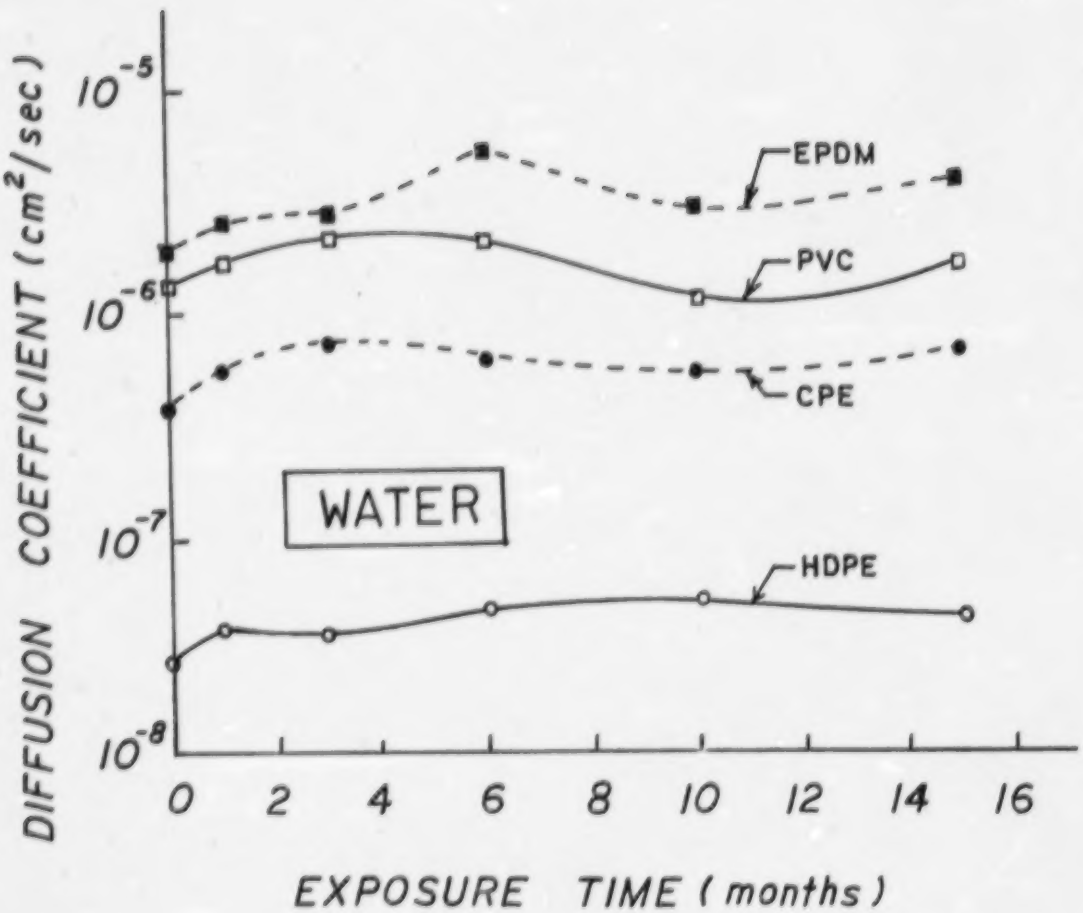


Figure 33 - Diffusion Coefficient Results for Various FML's as a Function of Water Exposure Time (15 month exposure)

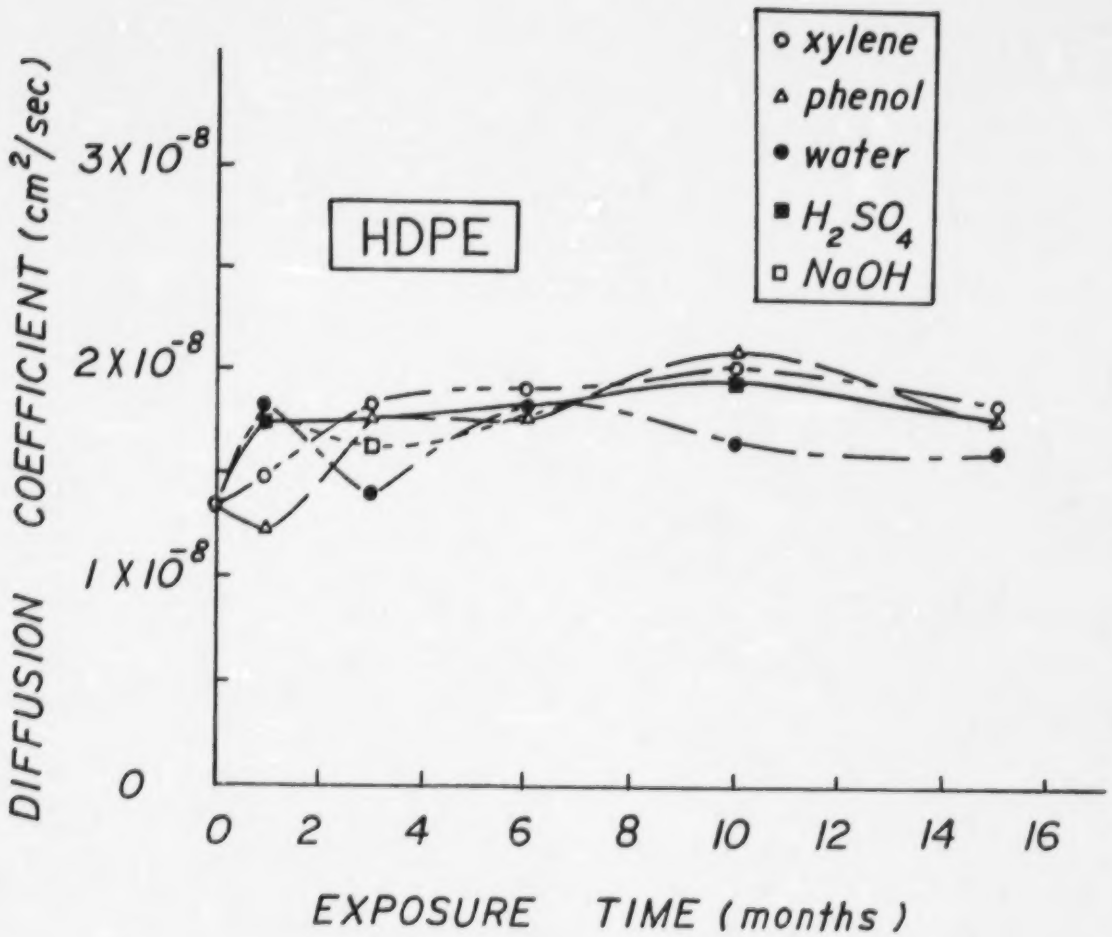


Figure 34 - Diffusion Coefficient Results as a Function of Chemical Exposure Time for HDPE (15 month exposure)

The results of Phase II are summarized in Table 8, where the changes between zero and fifteen months are given as well as the trend (up, down or steady) at fifteen months. The only situation that clearly indicates degradation is CPE exposed to phenol.

Table 8 - Summary of WVT, RT and BA Results for 15 Month Exposure

CPE	WVT	RT
H_2SO_4	- 28% - rising	+50% - decreasing
NaOH	- 25% - rising	+42% - decreasing
Phenol	+ 56% - rising	+100% - rising
Water	- 25% - steady	+44% - rising
HDPE	**WVT**	**RT**
H_2SO_4	-12.5% - rising	+23% - steady
NaOH	+12.5% - decreasing	+54% - rising
Phenol	+12.5% - steady	+23% - decreasing
Xylene	-12.5% - decreasing	+23% - steady
Water	-12.5% - rising	+23% - steady
FML's in Water	**WVT**	**RT or BA (HDPE)**
EPDM	0% - steady	+35% - steady
PVC	-5% - steady	+6% - steady
CPE	-29% - steady	+50% - steady
HDPE	0% - steady	+50% - steady

- First term is the change from as-received to the 15 month exposure value, e.g., -28%..
- Second term is the trend of the data at the 15 month mark, e.g., rising.

SECTION 7
QUALITY ASSURANCE

The seven aspects of quality assurance and quality control for environmentally-related measurements, as listed in the Federal Register, Vol. 48, No. 191, Friday, September 30, 1983, will be briefly discussed.

1 - The intended use of the data and the associated acceptance criteria for data quality control (precision, accuracy, representativeness, completeness, comparability).

The data is intended to be used as a basis for a possible method for predicting flexible membrane liner (FML) lifetime via transport measurements.

The data were judged acceptable because duplicate samples give results within 10% of each other in the testing methods ultimately used. Edge leakage effects were less than 5% of the bulk FML values in the water vapor transmission tests. Weighing was done to the nearest one hundredth of a gram.

The present values were compared wherever possible to values obtained from a very thorough literature search.

2 - Project requirements for prediction, accuracy, representativeness, completeness, comparability and how these will be determined.

Number 1 above applies here - as well as the following:

Representatives - FML's were the most widely used field types –

- thermosets - rubbers - EPDM
- thermoplastics - PVC, CPE and HDPE

Chemicals were of the general generic types –

- acids
- bases
- organic - aromatic
- water - as a control

and chosen from those types most commonly encountered in the field.

The FML's and chemicals were also quite compatible with those used in other similar type work sponsored by EPA (Bureau of Reclamation and National Sanitary Foundation).

Comparability - the results of the work were compared with the chemical compatibility literature of the FML producers as well as all other pertinent identified literature.

3 - Procedure for selection of samples or sampling sites and collection or preparation of samples.

The main consideration here was that exposure to the chemicals be one-sided as it would be in actual field situations. The samples were taken from flat portions, one-fold and two-fold regions of the exposed FML. Most of the work reported however was from the flat portions.

4 - Procedures for sample handling, identification, preservation, transportation and storage.

The FML's were taken from the exposure tubs, cut to the appropriate size for measurement and sealed in plastic bags. The bag was marked with proper identification with very tightly-adhering labels. Before the actual measurements, many samples were taken from the plastic bags and dessicated (dried) in a vacuum dessicator for one month to insure that they were in a completely dry ("chemical-free") state before measurements began.

5 - Description of measurement methods or test methods procedure with a statement of performance characteristics if methods are non-standard.

Will be covered in 7.6 below.

6 - Standard quality assurance/quality control procedures (e.g., ASTM or APHA standard procedures) to be followed. Non-standard procedures must be documented.

The water vapor transmission (WVT) tests were run with strict accordance to ASTM E-96-80 (Standard Method of Test for Water Vapor Transmission of Materials in Sheet Form).

There are no standard tests for diffusion coefficient measurements. The approach was to survey the literature very well and use the methods of testing which the majority of workers find the most satisfactory and reliable.

7 - Data reduction and reporting procedures, including description of statistical analyses to be used.

In both the water vapor transmission (WVT) and diffusion measurements, the data were analyzed by the appropriate equations using least square analysis. WVT results are reported in the customary (g/m^2-d) units and the diffusion coefficients in the usual (cm^2/sec) units. (The units can be converted to SI units with the conversion factors given in Appendix D.)

REFERENCES

1. Chain, E. S. K. and DeWall, F. B., "Sanitary Landfill Leachates and Their Treatment," Jour. Environ. Engr. Div., ASCE, Vo.. 102, No. EE2, Apr. 1976, pp. 411-431.

2. Kays, W. B., Construction of Linings for Reservoirs, Tanks and Pollution Control Facilities, J. Wiley and Sons, NY, 1977.

3. Koerner, R. M., Designing with Geosynthetics, Prentice-Hall, Englewood Cliffs, NJ, 1986.

4. Anderson, D. C., Brown, K. W. and Green, J., "Organic Leachate Effects on the Permeability of Clay Liners," Conf. Proc. Mgmt. of Uncontrolled Haz. Waste Sites, Washington, DC, Oct. 28-31, 1981, HMCRL, Silver Spring, MD, pp. 223-229.

5. Koerner, R. M., "Conceptual Design of Landfill Liners Using Synthetic Membranes," Proc. of Hazardous Materials Management Conf. and Exhib., Philadelphia, PA, July 14, 1983, Tower Conf. Mgmt. Co., Wheaton, Illinois.

6. Dougherty, R. H. and West, L. A., "Water Permeation Through Organic Materials," Sandia National Laboratories Report SAND 81-8250, September 1981.

7. Matsui, E. S., "Water Vapor Diffusion Through Protective Coatings, Part I. A Method of Measuring Water Vapor Permeability of Coating Films by Radioactive Tracer Technique and Its Application," U. S. Naval Civil Engineering Laboratory, Fort Hueneme, California, Technical Note N-922, Z-5011-01-01-087, October 1968.

8. Haxo, H. E., Jr. and Nelson, N. A., "Factors in the Durability of Polymeric Membrane Liners," Proc. Int'l. Conf. on Geomembranes, Denver, Colorado, June 20-24, 1984, Vol. II, pp. 287-292, publ. by IFAI, St. Paul, MN.

9. Bellen, G and Corry, R., "Chemical Resistance of Synthetic Liner/Hazardous Waste Combinations," Proc. 12th Annual Conf. on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, Cincinnati, Ohio, April 21-23, 1986, pp. 101-113. Sponsored by EPA Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio.

10. "Evaluation of Flexible Membrane Liner Seams After Chemical Exposure and Simulation Weathering," Bureau of Reclamation Report PB 87-166526, Denver, Colorado, Feb. 1987.

11. Emcon Associates, 1983, "Field Verification of Liners from Sanitary Landfills," EPA/9/-83-046, U. S. EPA, Cincinnati, Ohio, p. 32.

12. Haxo, H. E., 1983, "Analysis and Finger-printing of Unexposed and Exposed Polymeric Membrane Liners," In: Proceedings of the Ninth Annual Research Symposium: Land Disposal, Incineration, and Treatment of Hazardous Waste, EPA-600/9-83-018, U. S. EPA, Cincinnati, Ohio, pp. 157-171.

13. Haxo, H. E., R. M. White, P. D. Haxo, and M. A. Fong, 1982, Final Report: "Evaluation of Liner Materials Exposed to Municipal Solid Waste Leachate, U. S. EPA, Cincinnati, Ohio, NTIS No. PB 83-147-801.

14. Haxo, H. E., R. S. Haxo, N. A. Nelson, P. D. Haxo, R. M. White, and S. Dakessian, 1985, Final Report: "Liner Materials Exposed to Hazardous and Toxic Wastes," EPA-600/2-84-169, U. S. EPA, Cincinnati, Ohio, NTIS No. PB 85-121-333.

15. Matrecon, Inc., 1983, "Lining of Waste Impoundment and Disposal Facilities," SW-870 Revised, U. S. EPA, Washington, DC, 448 pp. GPO #005-00000231-2.

16. Nelson, N. A., H. E. Haxo, and Peter McGlew, 1985, "Recovery and Testing of a Synthetic Liner from a Waste Lagoon After Long-Term Exposure," In: Proceedings of the Eleventh Annual Research Symposium: Land Disposal of Hazardous Waste, EPA/600/0-85/013, U. S. EPA, Cincinnati, Ohio, pp. 196-306.

17. Roberts, S., N. A. Nelson, and H. E Haxo, 1983, "Evaluation of a Waste Impoundment Liner System After Long-Term Exposure," In: Proceedings of the Ninth Annual Research Symposium: Land Disposal, Incineration, and Treatment of Hazardous Waste, EPA-600/9-83-018, U. S. EPA, Cincinnati, Ohio, pp. 172-187.

18. Hulbert, L. E. and Mamoun, M. M., "A Perspective of Current Technology on the Time-Dependent Deformation and Fracture of Plastic Gas Piping Materials," Proc. Eighth Plastic Fuel Gas Pipe Symp., Nov. 29-30, Dec. 1, 1983, New Orleans, LA, pp. 4-8, publ. by American Gas Assn. (AGA).

19. Toll, K. G., Palermo, E. F. and Appleton, G. T., "Using Laboratory Tests on PE Piping Systems to Solve Gas Distribution Engineering Problems," Proc. Tenth Plastic Fuel Gas Pipe Symp., Oct. 27-29, 1987, New Orleans, LA, pp. 142-161, publ. by AGA.

20. Mruk, S. A., "Validating the Hydrostatic Design Basis of PE Piping Materials," Proc. 9th Plastic Fuel Gas Pipe Symp., New Orleans, LA, Nov. 12-14, 1985, pp. 202-214, publ. by AGA.

21. Leech, J. R., "Polyethylene Resins for Fuel Gas Piping Applications," Proc. 9th Plastic Fuel Gas Pipe Symp., New Orleans, LA, Nov. 12-14, 1985, pp. 3-16, publ. by AGA.

22. Our work, and also shown in the work of Haxo, H. E., Miedema, J. A. and Nelson, N. A., "Permeability of Polymeric Membrane Lining Materials," Proc. Int'l. Conf. Geomembranes, Denver, CO, June 20-24, 1984, publ. by IFAI, St. Paul, MN.

23. Crank, J. and Park. G. S., editors, Diffusion in Polymers, Academic Press, New York, 1968.

24. Southern, E. and Thomas, A. G, "Diffusion of Liquids in Crosslinked Rubbers," Rubber Chemistry and Technology, 42, pp. 495-504 (1969). They

mention the theory was developed by J. Crank, The Mathematics of Diffusion, Oxford University Press, 1956.

25. Joos, W., Diffusion in Solids, Liquids and Gases, Academic Press, New York, 1960, p. 25.

26. Carpenter, C. N. and Fisher, A. O., "Sequential Chemical Absorption Techniques for Evaluating Elastomers," Materials Performance, Vol. 20, No. 1, 1981, pp. 40-45.

27. Baker, G. R. and Thompson, G. M., "The Effect of Seawater on Polymers," NRL Memorandum Report 4097, Transducer Branch, Underwater Sound Reference Detachment, Orlando, Florida, November, 1979.

28. Brzozowski, K. J. and Kumins, C. A., "Barrier Properties of Earth Lining for Pollution Control," Proc. of Symp. on Permeability of Plastic Films and Coatings to Gases, Vapor and Liquids, Los Angeles, April, 1974, Plenum Press, NY, pp. 321-329.

APPENDICES

APPENDIX A

Details of ASTM E96-80 WVT Test

(a) Water Vapor Transmission (WVT) = $\frac{g \times 24}{t \times a}$

where

g = weight loss (grams)
t = time interval (days)
a = area of specimen (m^2)

(b) The permeance is given as

$$\text{Permeance} = \frac{WVT}{\Delta P} = \frac{WVT}{S(R_1 - R_2)}$$

where

ΔP = vapor pressure diff. across membrane (mm Hg)
S = saturation vapor pressure at test temperature (mm Hg)
R_1 = relative humidity in cup
R_2 = relative humidity outside cup (in environmental chamber)

(c) Permeability = Permeance x Thickness

Actual data from WVT test is shown in Figure 5 on page 16.

APPENDIX B

Actual Data From Water and Water Vapor Absorption Measurements

EPDM - Water Absorption

	D(cm^2/sec)	Equil. wgt. gained (%)
Control	0.91×10^{-9}	0.99

D-Values (cm^2/sec)

Chemical	1 Month	3 Months	6 Months
NaOH	2.8×10^{-9}	2.8×10^{-9}	1.3×10^{-9}
H_2SO_4	-	5.4×10^{-9}	-
Phenol	-	1.3×10^{-9}	0.44×10^{-9}
Xylene	1.9×10^{-9}	2.7×10^{-9}	-

Wgt. Gained in 20 Days (%)

NaOH	0.96	1.56	0.86
H_2SO_4	1.04	1.01	1.45
Phenol	-0.11	1.10	0.79
Xylene	1.50	1.51	-

Xylene not tested at 6 months.

EPDM - Water Vapor Absorption

	D(cm^2/sec)	Equil. wgt. gained (%)
Control	4.4×10^{-9}	0.23

D-Values (cm^2/sec)

Chemical	1 Month	3 Months	6 Months
NaOH	3.8×10^{-9}	2.7×10^{-9}	1.95×10^{-9}
H_2SO_4	5.3×10^{-9}	3.6×10^{-9}	-
Phenol	6.5×10^{-9}	3.5×10^{-9}	-
Xylene	1.9×10^{-9}	-	-

Wgt. Gained in 20 Days (%)

NaOH	0.35	0.40	0.13
H_2SO_4	0.33	0.33	0.15
Phenol	0.30	0.24	1.61
Xylene	0.25	0.56	-

Xylene not tested at 6 months.

Initial Temperature Dependence of Absorption (t^n)

n - values

EPDM - Vapor

Control-0.47

Chemical	1 Month	3 Months	6 Months
NaOH	0.31	0.27	0.41
H_2SO_4	0.32	0.01	0.31
Phenol	0.33	0.43	0.38
Xylene	0.28	0.12	-

EPDM - Liquid

Control-0.38

NaOH	0.42	0.40	0.42
H_2SO_4	0.43	0.37	0.63
Phenol	0.40	0.43	0.40
Xylene	0.43	0.62	-

PVC - Water Absorption

	D(cm^2/sec)	Equil. wgt. gained (%)
Control	-	0.01

D-Values (cm^2/sec)

Chemical	1 Month	3 Months	6 Months
NaOH H_2SO_4 Phenol Xylene	Weight gain is too scattered and equilibrium is not being reached. D-values cannot be determined.		

	Wgt. Gained in 20 Days (%)		
NaOH	0.01	1.20	-
H_2SO_4	1.63	1.35	-
Phenol	1.32	0.93	-
Xylene	-1.09	-0.51	-

PVC - Water Vapor Absorption

	D(cm^2/sec)	Equil. wgt. gained (%)
Control	-	0.05

D-Values (cm^2/sec)

Chemical	1 Month	3 Months	6 Months
NaOH H_2SO_4 Phenol Xylene	Weight gain is too small and scattered to obtain D-Values		

Wgt. Gained in 20 Days (%)

NaOH	0.02	0.07	-
H_2SO_4	0.16	0.13	-
Phenol	-0.40	0.03	-
Xylene	-1.98	-0.53	-

Initial Temperature Dependence of Absorption (t^n)

n - values

PVC - Vapor

Control –

Chemical	1 Month	3 Months	6 Months
NaOH	0.07	0.10	-
H_2SO_4	0.35	0.08	-
Phenol	-0.15	0.05	-
Xylene	-0.23	-	-

PVC - Liquid

Control 0.35

NaOH	0.25	0.31	-
H_2SO_4	0.44	0.40	-
Phenol	0.11	0.22	-
Xylene	-0.01	0.27	-

CPE - Water Absorption

	D(cm^2/sec)	Equil. wgt. gained (%)
Control	no final wgt.	-

D-Values (cm^2/sec)

Chemical	1 Month	3 Months	6 Months
NaOH H_2SO_4 Phenol	No final weight achieved in reasonable time of observation. No D-values possible.		

Wgt. Gained in 20 Days (%)

NaOH	3.4	5.22	3.4
H_2SO_4	4.45	5.25	3.9
Phenol	4.04	1.54	-3.0

Xylene destroys CPE in a few days.

CPE - Water Vapor Absorption

	D(cm^2/sec)	Equil. wgt. gained (%)
Control	2.1×10^{-9}	1.32

D-Values (cm^2/sec)

Chemical	1 Month	3 Months	6 Months
NaOH	1.57×10^{-9}	lost wgt.	lost wgt.
H_2SO_4	0.94×10^{-9}	no final wgt.	0.55×10^{-9}
Phenol	1.09×10^{-9}	lost wgt.	lost wgt.

Wgt. Gained in 20 Days (%)

NaOH	1.38	-0.028	-0.33
H_2SO_4	1.24	0.20	1.11
Phenol	3.0	-1.85	-2.6

$\overline{\text{X}}$ylene destroys CPE in a few days.

Initial Temperature Dependence of Absorption (t^n)

n - values

CPE - Vapor

Control - 0.54

Chemical	1 Month	3 Months	6 Months
NaOH	0.35	-1.3	-*
H_2SO_4	0.45	0.62	0.38
Phenol	0.38	-0.6	-*

CPE - Liquid

NaOH	0.34	0.48	0.43
H_2SO_4	0.58	0.53	0.38
Phenol	0.53	0.67	-*

*Losing weight

Reproduced from
best available copy.

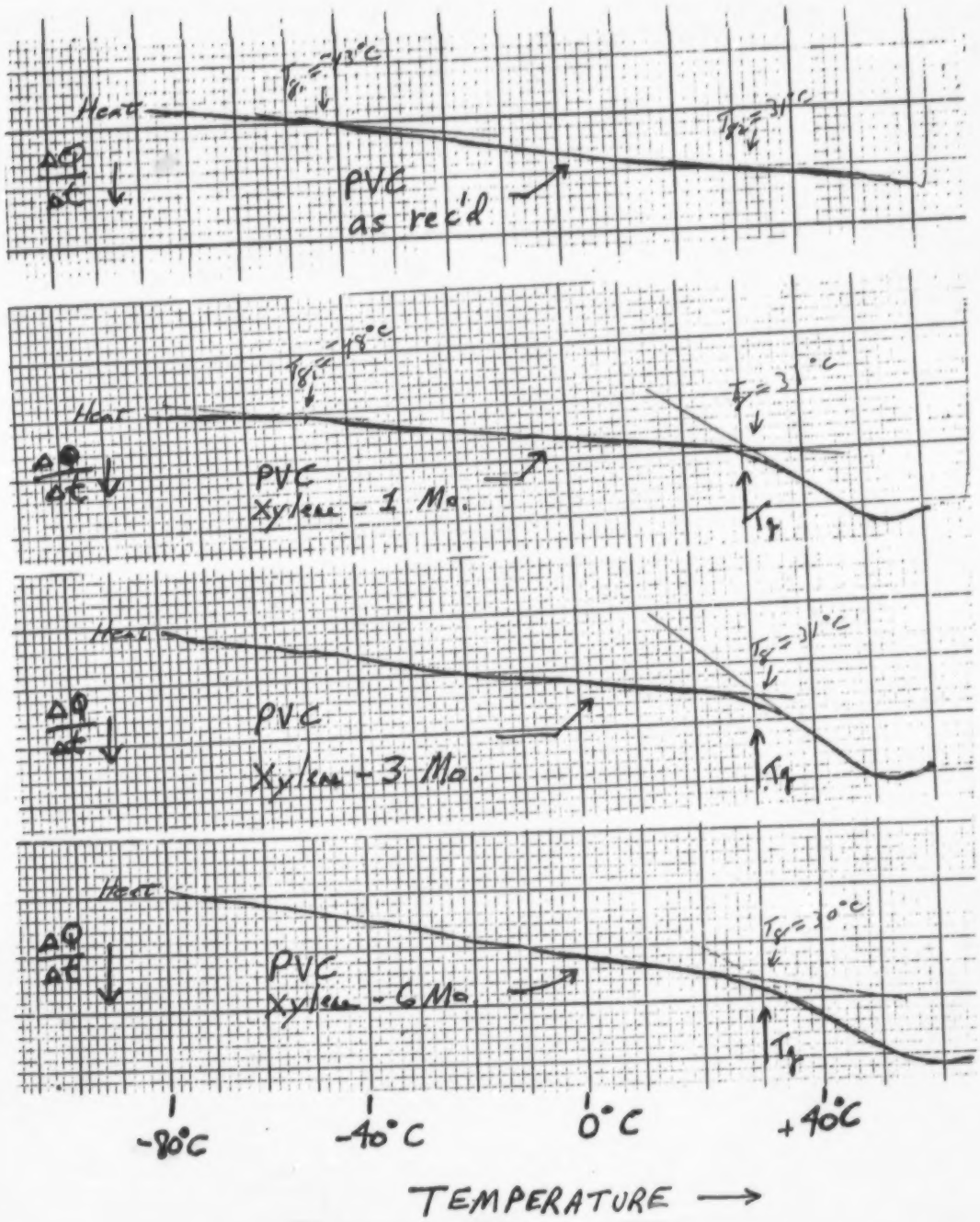


Figure 35 - Actual "Raw" Differential Scanning Calorimetry (DSC) Data for PVC Exposed to Xylene

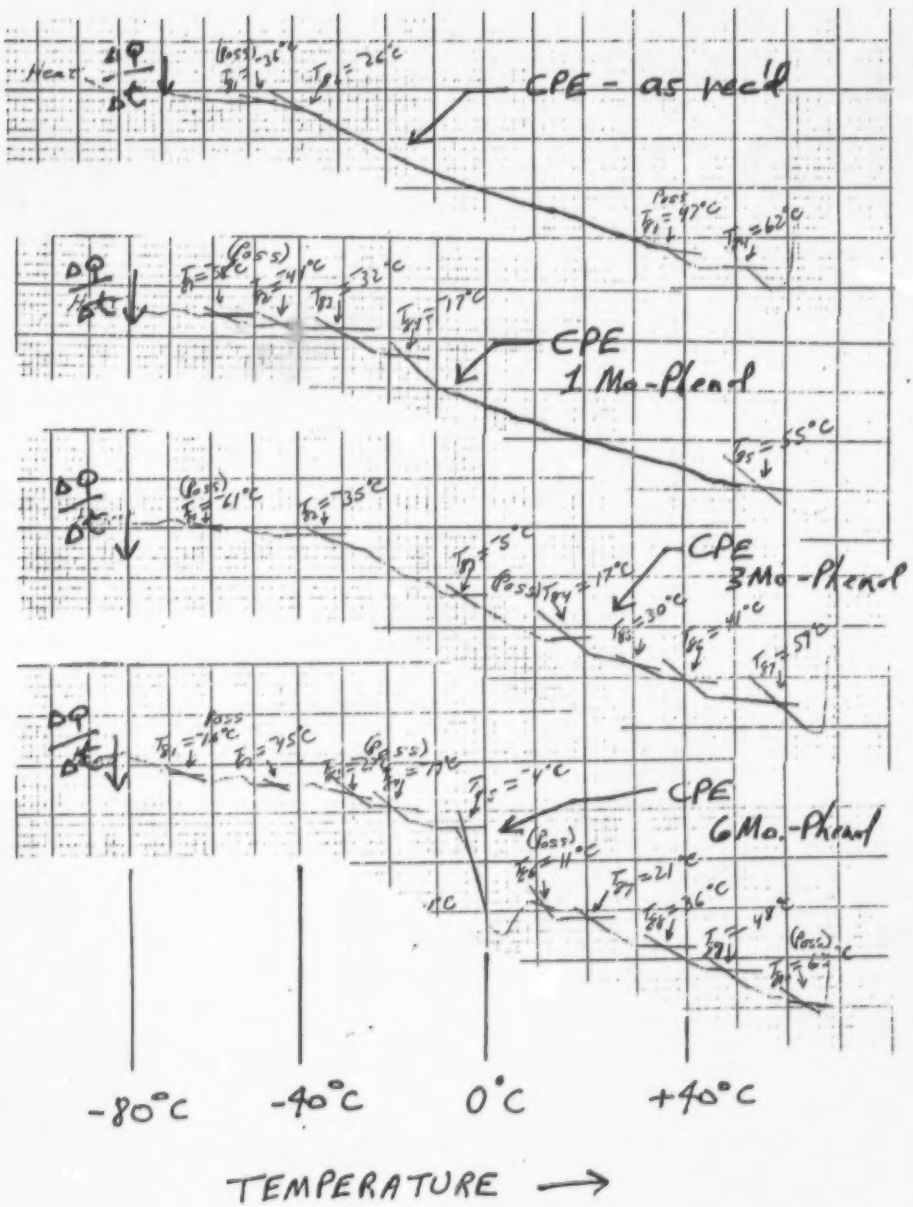


Figure 36 - Actual "Raw" DSC Data for CPE Exposed to Phenol

APPENDIX D

Unit Conversion Chart

Quantity Given In	MKS Unit	Conversion to Obtain MKS Unit
cm^2/sec	m^2/sec	multiply by 10^{-4}
feet	m	multiply by 0.3048
pounds/inch	N/m	multiply by 86.6
mil (0.001-inch)	m	multiply by 2.54×10^{-5}
days	sec	multiply by 8.64×10^{4}
inches	m	multiply by 2.54×10^{-2}
cm^2	m^2	multiply by 10^{-4}
gm	kg	multiply by 10^{-3}
gm/m^2-day	kg/m^2-sec	multiply by 1.16×10^{-8}
cm	m	multiply by 10^{-2}
months (30 days)	s	multiply by 2.59×10^{6}
cm/sec	m/sec	multiply by 10^{-2}